AUG 1 6 1924

ABSTRACTS

OF

CHEMICAL PAPERS

ISSUED BY THE

BUREAU OF CHEMICAL ABSTRACTS

JULY, 1924

BUREAU:

Chairman:

J. C. PHILIP, O.B.E., D.Sc., F.R.S.

Nominated by the Chemical Society:

C. S. GIBSON, O.B.E., M.A., M.Sc.
G. T. MORGAN, O.B.E., D.Sc., F.R.S.
J. F. THORPE, C.B.E., D.Sc., F.R.S.
W. P. WYNNE, D.Sc., F.R.S.

Nominated by the Society of Chemical Industry:

E. F. ARMSTRONG, D.Sc., F.R.S.
J. L. BAKER.
E. V. EVANS, O.B.E.
Sir W. J. POPE, K.B.E., F.R.S.

A. PURE CHEMISTRY

Editor:

T. F. BURTON, B.Sc.

Assistant Editors:

H. M. DAWSON, D.Sc., B.Sc., Ph.D.
A. A. ELDRIDGE, B.Sc.
W. E. GARNER, M.Sc.
H. J. PAGE, M.B.E., B.Sc.
E. H. RODD, D.Sc.
E. E. TURNER, M.A., D.Sc.
H. WREN, M.A., D.Sc., Ph.D.

Adviser on Nomenclature:

A. J. GREENAWAY.

Indexer:

MARGARET LE PLA, B.Sc.

OFFICES OF THE BUREAU:

CENTRAL HOUSE, 46, FINSBURY SQUARE, LONDON, E.C. 2

Organic Chemistry.

Pyrogenic Decomposition of Acyclic Hydrocarbons. H. GAULT, F. A. HESSEL, and Y. ALTCHIDJIAN (*Compt. rend.*, 1924, **178**, 1562—1565).—An introductory paper to the systematic study of the pyrogenic decomposition of acyclic hydrocarbons containing at least 16 carbon atoms, with special reference to the effects of temperature, rate of flow of liquid, and period of heating. The apparatus and procedure to be used are described. The preparation of hexadecene by the distillation of cetyl palmitate and of hexadecane by catalytic hydrogenation of hexadecene (cf. Brochet, A., 1914, i, 1069) is described. J. W. B.

Preparation of Acetylenic Hydrocarbons, their Sodium Derivatives, and the Corresponding Acetylenic Acids. L. MEUNIER and E. DESPARMET (*Bull. Soc. chim.*, 1924, [iv], **35**, 481—484; cf. A., 1907, i, 186).—Chloro derivatives of aliphatic aldehydes and ketones react with sodamide, giving the sodium derivatives of the corresponding acetylenic hydrocarbons. Acetylenic hydrocarbons react quantitatively with sodamide to give the corresponding sodium derivatives. Allyl and disubstituted acetylenic hydrocarbons react quantitatively on heating with sodamide, giving the sodium derivatives of the corresponding acetylenes. Ether and similar solvents play no useful part in the absorption of carbon dioxide by the sodium derivatives to form acids. A. B. H.

Partial Dehydration of Aldehydes and Ketones forming Acetylenic Hydrocarbons. BOURGUEL (*Compt. rend.*, 1924, **178**, 1557—1560).—The dehydrating and chlorinating action of phosphorus pentachloride on methyl *n*-propyl ketone, diethyl ketone, dipropyl ketone, heptaldehyde, acetophenone, and ethyl phenyl ketone, resulting in the formation of acetylenic and ethylenic compounds, is described. Methyl *n*-propyl ketone (1 mol.) treated in the cold with phosphorus pentachloride (1 mol.) forms Δ^{β}-pentinene, CEt:CMe (0·005 mol.), together with the compounds CHEt:CClMe (0·35 mol.), and CHEtCl·CHCl·CH_3 (0·06 mol.), the latter being detected by conversion into Δ^{β}-pentene by the action of zinc powder and alcohol; much hydrogen chloride is also evolved. It is assumed that it is the enolic form of the ketone which reacts with the phosphorus pentachloride. Diethyl ketone and dipropyl ketone yield the corresponding compounds, whilst heptaldehyde yields Δ^{α}-heptinene, C_5H_{11}·C:CH, and

chlorinated compounds. Neither acetophenone nor ethyl phenyl ketone gives acetylenic hydrocarbons. J. W. B.

Preparation of Two True Diacetylenic Hydrocarbons. LESPIEAU (*Compt. rend.*, 1924, **178**, 1565—1567).—On addition of αβ-dibromopropylene in ether to the product of the interaction of pentamethylene dibromide and magnesium shavings suspended in ether, a brisk reaction occurs and from the product, on repeated fractionation, the following compounds have been isolated: (1) Unchanged dibromopropylene; (2) Δ^{α}-*bromo-octene*, $Me\cdot[CH_2]_5\cdot CBr{:}CH_2$, b. p. 60—61°/11 mm., d^{20} 1·158, n_D 1·4715; (3) unchanged pentamethylene dibromide; (4) the alcohol, $CH_2{:}CBr\cdot[CH_2]_5\cdot CH_2\cdot OH$, b. p. 120—121°/11 mm., d^{21} 1·272, n_D 1·499 (*phenylurethane*, m. p. 52·5—53·5°); (5) βκ-dibromo-$\Delta^{\alpha\kappa}$-undecadiene, $CH_2{:}CBr\cdot[CH_2]_7\cdot CBr{:}CH_2$, b. p. 150—151°/10 mm., d^{25} 1·359, n_D 1·504; (6) βο-dibromo-$\Delta^{\alpha o}$-hexadecadiene, $CH_2{:}CBr\cdot[CH_2]_{12}\cdot CBr{:}CH_2$, b. p. 200—202°/10 mm., m. p. −5°, d^{20} 1·221, n_D 1·497. By the action of sodamide on (2) the octinene is obtained in more than 70% yield. By the action of alcoholic potash at the temperature of a water-bath on (5) $\Delta^{\alpha\kappa}$-*undecadi-inene*, $CH{:}C\cdot[CH_2]_7\cdot C{:}CH$, a liquid with an orange-like odour, b. p. 82·5—83°/12 mm., m. p. −17°, d^{21} 0·8182, n_D 1·453, is obtained which yields a yellow precipitate with ammoniacal cuprous chloride and a white *precipitate*, $C_{11}H_{14}Ag_2,2AgNO_3$, with alcoholic silver nitrate. Similar treatment of (6) yields $\Delta^{\alpha o}$-*hexadecadi-inene*, $CH{:}C\cdot[CH_2]_{12}\cdot C{:}CH$, brilliant laminæ, m. p. 44—45°, b. p. 152—155°/12 mm., giving corresponding *copper* and *silver* compounds. J. W. B.

Action of Inorganic Iodides on αβ-Dibromo Compounds. I. Mechanism of the Reaction. C. F. VAN DUIN (*Rec. trav. chim.*, 1924, **43**, 341—358).—The velocity of the reaction between metallic iodides and αβ-dibromo compounds, $R\cdot CHBr\cdot CHBr\cdot R' + 2M'I = R\cdot CH{:}CHR' + I_2 + 2M'Br$, has been measured at 25° in the dark in an atmosphere of carbon dioxide, using potassium iodide as the metallic iodide with αβ-dibromopropionic acid and αβ-dibromo-β-*p*-sulphophenylpropionic acid, respectively. The reaction appears to be termolecular, and it is probable that αβ-diiodo compounds occur as intermediate products which break down into ethylenic compounds and free iodine, with a velocity great compared with that of the substitution. Cations, except hydrogen ions, exert a strongly positive catalytic influence, and iodine ions act more rapidly than undissociated iodides. Light accelerates the reaction whilst iodine retards it. Calcium salts are slightly more active catalytically than potassium salts. E. H. R.

Spontaneous Combustion during Work with Dichloroethylene. H. THRON (*Chem.-Ztg.*, 1924, **48**, 142).—Spontaneous combustion due to chloroacetylene was observed during the distillation of a large quantity of alcohol containing about 0·25% of dichloroethylene, with sodium hydroxide. A. R. P.

Preparation of Alcohols of the Formulæ $R{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ and $R{\cdot}CR'H{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ and the Corresponding Acids, starting with Aldehydes, R·COH, and Ketones, R·CO·R'. A. VERLEY (*Bull. Soc. chim.*, 1924, [iv], **35**, 487—488).—Condensation of an aldehyde and a ketone in presence of sodium ethoxide gives rise to an ester of the type $R{\cdot}CH\!-\!CH{\cdot}CO_2Et$ (O), which, by reduction with sodium and alcohol, gives the alcohol, $CH_2R{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, and by hydrolysis followed by reduction, the acid $CH_2R{\cdot}CH_2{\cdot}CO_2H$. A. B. H.

Catalytic Decomposition of Ethyl Alcohol in the Presence of Alumina. J. E. GORIS (*Chim. et Ind.*, 1924, **11**, 449—452).—Ethyl alcohol is decomposed into ethylene and water when its vapour is passed over alumina heated at 430—450°; a small quantity of hydrogen (about 4·5% of the ethylene) is also produced, and the formation of hydrogen increases rapidly with increase of temperature above the limit mentioned. The volume of ethylene produced is a measure of the amount of alcohol, and the reaction may be used for the determination of alcohol in mixtures of alcohol and benzene, since the latter is not decomposed by the catalyst. To prepare the catalyst, a mixture of equal weights of aluminium hydroxide and pumice-stone is powdered and heated for 1 hour at 300°. W. P. S.

Chlorination of Ethyl Alcohol. F. D. CHATTAWAY and O. G. BACKEBERG (*J. Chem. Soc.*, 1924, **125**, 1097—1101).—The initial stage in the chlorination of ethyl alcohol consists in the formation of ethyl hypochlorite, which then reacts with the excess of alcohol to yield acetaldehyde. The latter undergoes a series of changes resulting in the successive formation of (*inter alia*) monochloroacetaldehyde alcoholate, trichloroethyl ether, dichloroacetaldehyde alcoholate, and finally chloral alcoholate. C. J. S.

Stepwise Oxidation of Citronellol and Geraniol. A. KOTZ and T. STECHE (*J. pr. Chem.*, 1924, [ii], **107**, 193—210; cf. Verley, A., 1919, i, 146).—The regulated oxidation of citronellol and geraniol yields formic acid, thus pointing to the presence of the group $CH_2{:}CMe{-}$. Citronellol, treated with perbenzoic acid (Prileschaeff, A., 1912, i, 633), gives *oxidocitronellol*, $C_{10}H_{20}O_2$, an oil, b. p. 139—140°/13 mm., d_4^{20} 0·9439, n_D^{20} 1·45519, in nearly theoretical yield. This product is rapidly hydrolysed by dilute sulphuric acid to dihydroxyhydrocitronellol, which, oxidised with ice-cold alkaline potassium permanganate solution, gives an oily substance, possibly *α-hydroxy-αε-dimethylsuberic acid*; the latter substance at 30° breaks up into formic acid and a heavy oil. Dihydroxyhydrocitronellol oxidised with cold chromic acid yields acetic acid, a little acetone, and β-methyladipic acid.

When geranyl acetate is oxidised in ice-cold solution with potassium permanganate, *dihydroxygeraniol oxide acetate*, m. p. 106—106·5°, is obtained, which is hydrolysed to *dihydroxygeraniol oxide*, m. p. 99°. The latter, treated with ice-cold potassium perman-

ganate, gives an oily acid, possibly *αεζ-trihydroxy-αε-dimethylsuberic acid*, which at 30° rapidly breaks up into formic acid and a ketonic compound, yielding a *phenylhydrazone*, m. p. 166—167°. The same end-products were obtained by oxidising geraniol dioxide or geraniol itself in the same way. W. A. S.

Complex Compounds of Bivalent Platinum with Organic Disulphides and Polysulphides. L. TSCHUGAEV and S. ILJIN [Edited by E. FRITZMANN] (*Z. anorg. Chem.*, 1924, **135**, 143—152). —β-*Dimethyltrimethylene diethyl dithioether*, $CMe_2(CH_2{\cdot}SEt)_2$, prepared by the action of sodium mercaptide on pentaglycol, when shaken for 3 hours with an aqueous solution of potassium chloroplatinate, gives an insoluble rose-coloured *powder*, $\left[C_9H_{20}\right]^{-S}_{-S}{>}PtCl_2$, which reacts with salts of Rieset's base; on heating, it yields a yellow form, m. p. 218—219°, soluble in alcohol, giving no reaction with Rieset's salts, to which the structure $\left[(C_9H_{20})^{-S}_{-S}{>}Pt{<}^{S-}_{S-}(C_9H_{20})\right]PtCl_4$ is assigned.

Pentaerythrityl ethyl thioether, $C(CH_2{\cdot}SEt)_4$, b. p. 216—218°/14 mm., when shaken with the chloroplatinite solution in the cold yields a yellow insoluble *compound*, $PtCl_2{<}^{SEt{\cdot}CH_2}_{SEt{\cdot}CH_2}{>}C{<}^{CH_2{\cdot}SEt}_{CH_2{\cdot}SEt}$. If the reaction mixture is heated, a mixture is produced of this substance and a *compound*, $\left(PtCl_2{<}^{SEt-CH_2-}_{SEt-CH_2-}\right)_2C$.

Acetylene diethyl dithioether, SEt·CH:CH·SEt, reacts very rapidly in the cold with potassium chloroplatinate solution, giving a rose-coloured powder which quickly changes to a yellow form. S. I. L.

Complex Compounds of Palladium with Organic Mono- and Di-sulphides. L. TSCHUGAEV and C. IWANOV [Edited by E. FRITZMANN] (*Z. anorg. Chem.*, 1924, **135**, 153—160).—The additive compounds of diethyl sulphide with palladium dichloride have been re-examined, and the descriptions of Ardell (*ibid.*, 1897, **14**, 143) and of Phillips (A., 1901, i, 444) confirmed except in the following particulars: $PdCl_2,2Et_2S$, m. p. 82°; $PdBr_2,2Et_2S$, m. p. 100°; $PdI_2,2Et_2S$, m. p. 104°. The solubilities in *iso*pentane at 25° have been determined.

With the ethylene diethyl dithioether, $SEt{\cdot}CH_2{\cdot}CH_2{\cdot}SEt$, an analogous series of compounds has been obtained. The *chloride*, $PdCl_2,C_6H_{14}S_2$, m. p. 180°, *bromide*, m. p. 159°, and *iodide*, m. p. 154°, exist in one form only.

The action of carbon monoxide on complex palladium compounds has been examined; whilst the ammoniacal compounds are readily reduced, the sulphide compounds are less readily and the disulphide compounds only with difficulty reduced; the speed of reduction varies with the solubility. S. I. L.

Application of Thallium Compounds in Organic Chemistry. I. Thallous Hydroxide. R. C. MENZIES and E. M. WILKINS (*J. Chem. Soc.*, 1924, **125**, 1148—1152).—A standard solution of

thallous hydroxide may be used for the titration particularly of organic acids. The thallous salts of organic acids are considerably less soluble than those of the alkali metals, are readily crystallised, and hence can be used as a convenient means of isolation and purification. Several new thallous salts are described. The *palmitate* (feathery aggregates from ethyl alcohol) and the *oleate* (white needles) both behave as soaps in dilute aqueous solution. Normal *thallous adipate*, crystalline leaflets, *normal pimelate*, long needles, and *hydrogen pimelate*, prisms, m. p. 137—140°, have also been prepared. The *thallous* salt of ethyl acetonedicarboxylate forms minute needles, m. p. 125° (decomp.). Thallous hydroxide dissolves isatin and yields yellow needles of *thallous isatate*, decomp. 148°.

Thallous hydroxide gives coloured solutions when heated with reducing sugars, thus resembling sodium hydroxide; further heating causes reduction with the formation of thallium mirrors. Non-reducing sugars are not affected. C. J. S.

Basic Zinc Acetate Analogous to the Beryllium Salt. V. Auger and (Mlle.) I. Robin (*Compt. rend.*, 1924, **178**, 1546—1548).—Whereas the distillation of zinc acetate under atmospheric pressure or in a moderate vacuum furnishes the normal salt mixed with decomposition products, distillation in a high vacuum gives, in a pure state, the *basic* salt, $Zn_4O(CH_3CO_2)_6$, which crystallises in transparent octahedra, m. p. 249—250°, decomposed by water and by absolute alcohol. Urbain and Lacombe (A., 1902, i, 132) obtained the corresponding salt of beryllium, and the formation of this volatile basic zinc salt demonstrates the close analogy between beryllium and zinc (cf. Lacombe, A., 1902, i, 418). J. W. B.

Heterogeneous Catalysis. I. Selective Action of the Nickel Catalyst in the Hydrogenation of certain Vegetable Oils. A. S. Richardson, C. A. Knuth, and C. H. Milligan (*Ind. Eng. Chem.*, 1924, **16**, 519—522).—The hydrogenation of cotton seed, arachis, and soya bean oils is characterised by the preferential conversion of linoleic acid to oleic acid and its isomerides. The selective hydrogenation of linoleic acid appears to be more marked when increasing amounts of the nickel catalyst are used and when the temperature is increased up to an optimum of about 200°. It appears to be well established that the normal course of hydrogenation of a single unsaturated component of a liquid mixture involves a constant rate of hydrogen absorption as long as the concentration of that component exceeds a fairly well-defined critical value. Owing to the selective action of the catalyst, a constant rate of hydrogen absorption is not uncommon, even when the reaction mixture contains a variety of unsaturated components. H. C. R.

Catalytic Hydrogenation of Oleic Acid and Commercial Olein with Nickel as Catalyst. de Roubaix (*Bull. Soc. chim. Belg.*, 1924, **33**, 193—212).—Oleic acid and commercial olein may be completely hydrogenated, after purification by distillation under

diminished pressure, by means of a rapid current of hydrogen at atmospheric pressure in the presence of 4% of reduced nickel as catalyst, the temperature being between 160° and 230°. The catalyst should not be prepared within the material to be hydrogenated, as this leads to considerable formation of nickel oleate, which encloses the nickel particles and inhibits their action. The presence of sulphur in non-distilled olein poisons the catalyst. [Cf. *B.*, July 25th.] W. T. K. B.

Preparation of Solutions of Acetoacetic Acid. G. Ljungren (*Biochem. Z.*, 1924, **145**, 422—425).—A 2% excess of sodium hydroxide solution warmed to 25° is placed in a flask which has been blown out with air free from carbon dioxide, and a weighed quantity of methyl acetoacetate is added. Hydrolysis is complete in 250 minutes and the solution is then neutralised with hydrochloric acid or by passing a stream of carbon dioxide for 10 minutes. The solution is 0·3% less concentrated than theory demands. The methyl alcohol resulting from the hydrolysis may be removed by aëration in a vacuum with pure air. Under similar conditions, ethyl acetoacetate is hydrolysed in 375 minutes. Kept over ice, such solutions decrease in concentration by 0·15% *per diem*. J. P.

Pyrogenic Dissociation of Sodium Oxalate. S. Ott (*Z. physikal. Chem.*, 1924, **109**, 1—33).—The thermal decomposition of sodium oxalate, obtained by heating sodium formate, into sodium carbonate and carbon monoxide has been studied. At all temperatures at which an appreciable decomposition takes place, even as low as 160°, there is a further reaction by which the carbon monoxide gives carbon dioxide and carbon, which accelerates the further evolution of gas. Hydrogen always appears in the residual gases, probably derived from traces of water which are difficult to remove from the oxalate. The equilibrium pressure has not been reached experimentally in a single case. Heating sodium carbonate under a pressure of 1100 atmospheres of carbon monoxide (which is greatly in excess of the calculated pressure) failed to reverse the process. This result seems to indicate that the decomposition of sodium oxalate by heat is still another example of an irreversible equilibrium. M. S. B.

Stereochemistry of Ruthenium. R. Charonnat (*Compt. rend.*, 1924, **178**, 1279—1282).—Complex salts of ruthenium have been studied on the basis of the Werner theory of co-ordination. The compound $2[Ru(C_2O_4)_3]K_3,KCl,8H_2O$, which is perfectly hexa-co-ordinated, was prepared by treating $RuCl_3,HCl,2H_2O$ with a slight excess of normal potassium oxalate for 2 hours at 130°. By recrystallisation from water, the salt, $[Ru(C_2O_4)_3]K_3,4{\cdot}5H_2O$, was obtained. These compounds are isomorphous with corresponding compounds of iridium and rhodium. Resolution was attempted by crystallisation of the double salt with *d*-potassium iridiotrioxalate. The active ruthenotrioxalate, however, either racemised immediately on liberation or possessed nearly zero

rotatory power. The compound $[Ru(NO)en_2I]I_2,2H_2O$ was transformed by prolonged heating into a salt of the same molecular composition, but crystallising in the anhydrous form. This compound and the series derived from it must possess the *cis* configuration if the series prepared by Werner and Smirnoff (A., 1921, i, 13) possesses the *trans* configuration. A. B. H.

Stereochemistry of Ruthenium. R. CHARONNAT (*Compt. rend.*, 1924, **178**, 1423—1426; cf. preceding abstract).—The action of normal potassium oxalate (2 mols.) on Joly's salt, $[Ru(NO)Cl_5]K_2$, yields a highly soluble *potassium ruthenochloronitrosodioxalate*, $[Ru(NO)Cl(C_2O_4)_2]K_2$, which is prone to supersaturation and with alkaloids forms salts incapable of crystallising. The replacement of an atom of chlorine in the complex anion by a molecule of pyridine lowers the solubility and yields a more tractable compound. *Potassium ruthenonitrosopyridinodioxalate*, $[Ru(NO)C_5H_5N(C_2O_4)_2]K$, prepared by the successive action of potassium oxalate and pyridine on $[Ru(NO)Cl_5]K_2$, forms large, red, triclinic plates ($+4H_2O$), and by hydrochloric acid at 100° is converted into the complex $[Ru(NO)C_5H_5NCl_4]$. The latter, under the action of pyridine, gives the compound $[Ru(NO)(C_5H_5N)_2Cl_2(OH)]$, and this yields the compound $[Ru(NO)(C_5H_5N)_2Cl_3]$ (I), when treated with hydrochloric acid. Compound (I) is obtained also by the action of hydrochloric acid on the compound $[Ru(NO)(C_5H_5N)_2Cl(C_2O_4)]$, which is another product of the action of potassium oxalate and pyridine on the salt $[Ru(NO)Cl_5]K_2$. All these compounds are highly stable.

By double decomposition with quinine hydrochloride, potassium ruthenonitrosopyridinodioxalate yields two isomeric, pink quinine salts of different solubilities, the one dextro- and the other lævorotatory; the quinidine salts behave similarly, but most of the alkaloids yield uncrystallisable salts. In aqueous solution, the corresponding ammonium salts have $[\alpha]_D$ $\pm 425°$, and from a solution containing a mixture of the two a crystalline racemic salt may be obtained. The active pyridine salts were also obtained crystalline. T. H. P.

Condensation Reactions involving Elimination of Ester Groups. L. SOUTHER (*J. Amer. Chem. Soc.*, 1924, **46**, 1301—1305).—Methylene iodide condenses with methyl and ethyl phenylmalonates in presence of sodium methoxide with formation, respectively, of *methyl* αγ-*diphenylglutarate*, b. p. 205—210°/6 mm., and *ethyl* αγ-*diphenylglutarate*, b. p. 216—217°/7 mm., and elimination of methyl and ethyl carbonates. A new *isomeride* of αγ-diphenylglutaric acid, m. p. 185—186·5°, together with the ordinary modification, was obtained by saponification of the methyl ester with sodium methoxide. With ethyl phenylcyanoacetate, methylene iodide yields similarly αγ-diphenylglutaronitrile. F. G. W.

Rotatory Dispersion of Tartaric Acid. L. LONGCHAMBON.—(See ii, 373.)

Decomposition of Dihydroxymaleic Acid. A. LOCKE (*J. Amer. Chem. Soc.*, 1924, **46**, 1246—1252).—An attempted synthesis of optically active sugars by the decomposition of the quinine salt and menthyl ester of dihydroxymaleic acid failed because the rate of polymerisation of the glycollaldehyde first formed was so slow in comparison with that of the decomposition of the dihydroxymaleic acid that the orientating effect of the quinine and menthol was lost. An attempt to catalyse the condensation of the aldehyde by means of alkalis showed that the sodium and potassium salts of dihydroxymaleic acid are relatively stable in solution, and that the addition of pyridine induces rapid decomposition of the otherwise stable solution of dihydroxymaleic acid in chloroform or benzene. The rates of decomposition of dihydroxymaleic acid and its disodium salt were measured in aqueous solution at 25°, by determining at intervals the glycollaldehyde produced. The experimental values for the unimolecular constant of the reaction are in accordance with the hypothesis that decomposition proceeds through the solvated, non-ionised, carboxyl group.

F. G. W.

Biological Oxidation. I. Absorption of Oxygen by the System Linoleic Acid–SH Group. A. VON SZENT-GYÖRGYI (*Biochem. Z.*, 1924, **146**, 245—253).—The product resulting from the catalytic oxidation of linoleic acid by thioglycollic acid in the presence of oxygen has been isolated as a dark yellow, viscous oil, which appears to be a compound of the ethylene oxide type, and not a peroxide, as supposed by Meyerhof (*Pflüger*, 1923, **199**, 531).

J. P.

Biological Oxidation. II. Mechanism and Significance of SH-Catalysis. A. VON SZENT-GYÖRGYI (*Biochem. Z.*, 1924, **146**, 254—258).—From a comparison of the oxidative action of thioglycollic acid and of ethyl peroxide on various aliphatic acids in the presence of air and an iron catalyst, it is concluded that thioglycollic acid combines with the oxygen of the air to form an active peroxide.

J. P.

***n*-α-Sulphobutyric Acid and its Optically Active Components.** H. J. BACKER and J. H. DE BOER (*Rec. trav. chim.*, 1924, **43**, 297—315).—An extended account of work previously published in an abbreviated form (A., 1923, i, 536). *Lead* α-*sulphobutyrate* crystallises in small needles with $2H_2O$; a *basic* salt has the composition $C_4H_6O_5SPb_2(OH)_2$. *Copper* α-*sulphobutyrate* forms a pale blue crystalline powder containing $1H_2O$; the *copper hydrogen*, *nickel*, and *cobalt* salts are also described. Two *strychnine* salts are described, the *normal* salt, small, glistening needles, m. p. 226—227°, and the *hydrogen* salt, aggregates of small, white needles. The two corresponding *brucine* salts and the normal *quinine* salt were obtained. Both the strychnine and quinine salts were used for the resolution of α-sulphobutyric acid, the former depositing first the salt of the *d*-acid, whilst the latter deposited the salt of the *l*-acid in excess. The pure components of α-sulphobutyric acid

have $[\alpha]_D$ ±7·8° and the normal barium salts, ±29·6°. The acid salts, in which the carboxyl group is probably free, have the same sign of rotation as the free acids, the value being about ±4°. The rotation-dispersions of the acid and its salts are normal, except for the coloured salts in alcohol. E. H. R.

Condensation of Aldehydes with Ammonia in Presence of Alumina. A. E. TSCHITSCHIBABIN (*J. pr. Chem.*, 1924, [ii], **107**, 129—131).—Further details of work already published (this vol., i, 312). W. A. S.

Sodium Hydroxylaminesulphonate as a Reagent for the Preparation of Oximes. W. L. SEMON and V. R. DAMERELL (*J. Amer. Chem. Soc.*, 1924, **46**, 1290—1293).—Sodium hydroxylaminemonosulphonate forms a convenient reagent for the preparation of oximes in acid solution. The ketone is heated at 70—100° with the theoretical quantity of the sodium monosulphonate in aqueous solution (1·29 mols. per litre), made alkaline in the cold, and the oxime extracted with a solvent. Negative results were obtained with benzil and quinonemonoxime. F. G. W.

Reduction of Citronellal. H. RUPE and R. RINDERKNECHT (*Helv. Chim. Acta*, 1924, **7**, 541—546).—Citronellal was reduced by von Braun and Kaiser (this vol., i, 3) to dihydrocitronellol ($\gamma\eta$-dimethyloctanol), $[\alpha]_D$ +2·38°, a value only about one-half that of citronellol, $[\alpha]_D$ +4·17°. This contradicts the authors' rule that a double bond so far removed from the asymmetric carbon atom as that in citronellol should have practically no effect on the rotation. The authors have therefore repeated the reduction of citronellal, using the nickel catalyst previously described (A., 1919, i, 29). The dihydrocitronellol had n_D 1·43417, $[\alpha]_D$ +4·09°, from which it is concluded that the preparation of von Braun and Kaiser, obtained by reduction under pressure at 150°, was impure. Both citronellol and dihydrocitronellol show slightly anomalous rotation dispersion. E. H. R.

Carbohydrates and Polysaccharides. IX. Synthesis of 2 : 3-Dimethyl*cyclo*pentenaldehyde. R. R. READ and H. HIBBERT (*J. Amer. Chem. Soc.*, 1924, **46**, 1281—1283).—*β-Bromobutaldehyde diethyl acetal*, $CHMeBr{\cdot}CH_2{\cdot}CH(OEt)_2$, a heavy, yellow, unstable oil, b. p. 82—85°/12—15 mm., was obtained by the addition of crotonaldehyde to alcoholic hydrobromic acid. This was treated with magnesium in ether, and the product decomposed with dilute sulphuric acid. The oil obtained was identical with the 2 : 3-dimethyl*cyclo*pentenaldehyde obtained by the electrolytic reduction of crotonaldehyde (this vol., i, 613). Its formation is to be represented by the elimination of water from dimethyladipaldehyde, the acetal of which is formed by the elimination of bromine from two molecules of β-bromobutaldehyde diethyl acetal by the action of the magnesium. A similar synthesis could not be carried out with the corresponding chlorine compound. F. G. W.

Carbohydrates and Polysaccharides. X. Synthesis and relative Stability of Cyclic Acetals from αβ- and αγ-Glycols. H. HIBBERT and J. A. TIMM (*J. Amer. Chem. Soc.*, 1924, **46**, 1283—1290).—The relative stability and ease of formation of 5- and 6-membered cyclic acetals were measured by allowing an αβ- and an αγ-glycol to condense competitively with various aldehydes in presence of dilute sulphuric acid at 100°, and measuring the yields of the two cyclic acetals formed when equilibrium had been reached. In the cases examined, the end-product contained a preponderance of the 6-membered derivative, the preponderance being greater the higher the molecular weight of the aliphatic aldehyde employed. A mixture of ethylene and trimethylene glycols (1 mol. of each) condensed with 1 mol. of paracetaldehyde, *n*-butaldehyde, *n*-heptaldehyde, and benzaldehyde, respectively, to form the 5- and 6-membered cyclic acetals in the respective proportions 1 : 1·8, 1 : 6·6, 1 : 7·3, and 1 : 2·1. Similar partition experiments, using ethylene glycol (1 mol.) and a mixture of benzaldehyde (1 mol.) with paracetaldehyde, *n*-butaldehyde, or *n*-heptaldehyde (1 mol.) gave ratios of the yields of products from benzaldehyde to those from the aliphatic aldehydes of 1 : 3·6, 1 : 1·2, and 1 : 0·7, respectively. Using trimethylene glycol, the corresponding ratios were 1 : 6·2, 1 : 4·4, and 1 : 2·0, the stability of cyclic acetals from aliphatic aldehydes decreasing with increasing molecular weight. The n-*butylidene ether*, b. p. 132—136°, and *benzylidene ether*, b. p. 225°, of ethylene glycol and the n-*butylidene ether*, b. p. 154—157°, of trimethyleneglycol are described. The cyclic acetals are readily hydrolysed by water or dilute acids, are more stable to alkalis, and very resistant to permanganate in acetone.

F. G. W.

Application of Azeotropy to the Preparation of Organic Compounds. H. WUYTS (*Bull. Soc. chim. Belg.*, 1924, **33**, 167—192).—A general discussion of the vapour pressures and boiling points of liquid binary mixtures, and a recapitulation of previous work on esterification (A., 1921, i, 494) and etherification (A., 1923, i, 532). Similar methods are described for the preparation of formals. In each case, the lower members of the homologous series are obtained directly as the most volatile component or as the predominant constituent of a binary mixture. With the higher members, the separation is facilitated by the heterogeneity of the mixture, and water is eliminated in the form of a binary mixture with alcohol.

W. T. K. B.

Preparation of Acetals from Aldehydes and Ketones. B. HELFERICH and J. HAUSEN (*Ber.*, 1924, **57**, [*B*], 795—799).—Acetals may be obtained by the action of orthosilicic esters (1·1 mols.) on solutions of aldehydes or ketones (1 mol.) in the requisite anhydrous alcohol (2—3 mols.) in the presence of hydrogen chloride; the mixtures are preserved for some days at the atmospheric temperature or heated under a reflux condenser. Unchanged ester is removed, if necessary, by treating the products with potassium hydroxide. The new method is not more advantageous than

Fischer's process in those cases in which the latter gives good yields, but is superior to that involving orthoformic esters, since the materials are more readily prepared, and, in certain cases, it is possible to transform unsaturated aldehydes and ketones into acetals without addition of alcohol at the double bond. The following compounds are described: lævulinaldehyde (keto)-dimethylacetal, b. p. 76—80°/10 mm., d_4^{20} 0·9713, n_D^{20} 1·4203; the derivatives of *cyclo*hexanone: *dimethylacetal*, b. p. 54—56°/13 mm., $d_4^{19\cdot2}$ 0·9528, $n_D^{19\cdot2}$ 1·4416; *diethylacetal*, b. p. 75—76°/13 mm., $d_4^{17\cdot5}$ 0·9156, $n_D^{17\cdot5}$ 1·4452; *diallylacetal*, b. p. 106—108°/13 mm., $d_4^{17\cdot5}$ 0·9410, $n_D^{17\cdot5}$ 1·4632; *diisobutylacetal*, b. p. 115—116°/13 mm., d_4^{15} 0·8927, n_D^{15} 1·4413; *diisoamylacetal*, b. p. 138—140°/12 mm., $d_4^{18\cdot5}$ 0·9165, $n_D^{18\cdot5}$ 1·4605; *benzaldehyde cetylacetal*; *crotonaldehyde dimethylacetal*, b. p. 124—128°/760 mm., d_4^{18} 0·8829, n_D^{18} 1·4130; *methylheptenone dimethylacetal*, b. p. 80—83°/14 mm., d_4^{18} 0·8770, n_D^{18} 1·4380.

The requisite orthosilicic esters are prepared by gradually adding silicon tetrachloride (1 mol.) to the well-cooled alcohol (4·4 mols.) and subsequently slowly heating the mixture to its boiling point if this does not exceed 150° and keeping it at this temperature until hydrogen chloride ceases to be evolved. The final traces of acid are removed by treatment of the product with a solution of sodium ethoxide in alcohol. The following new esters are described: *tetra-allyl orthosilicate*, b. p. 115—116°/13 mm., d_4^{17} 0·9842, n_D^{17} 1·4347; *tetrabenzyl orthosilicate*, long needles, m. p. 32·5°, b. p. 305°/12 mm.; *tetracyclohexyl orthosilicate*, needles, m. p. 88·5°, b. p. 230—240°/11 mm.; *tetra-acetyl orthosilicate*, m. p. 46·5—48·5°. Tetramethyl, tetraethyl, tetra*iso*butyl, and tetra*iso*amyl orthosilicates have b. p. 25—27°/12 mm., 60—62°/12 mm., 129—131°/13 mm., and 173—176°/12 mm., respectively. *Methyl silico-orthoformate*, b. p. 104—106°/760 mm., is prepared in 66% yield from methyl alcohol and trichlorosilane. H. W.

Additive Products of Methyl Ethyl Ketone with Chloroform, Bromoform, and Iodoform. B. Ekeley and C. J. Klemme (*J. Amer. Chem. Soc.*, 1924, **46**, 1252—1254).—Chloroform, bromoform, and iodoform (2 mols.) condense, respectively, with methyl ethyl ketone (1 mol.) in presence of dry, powdered potassium hydroxide, with formation of *trichloro*-tert.-*amyl alcohol*, b. p. 110—113°/620 mm. (decomp.), d_4^{20} 1·2128, n_D^{20} 1·4460, M_D 42·107; *tribromo*-tert.-*amyl alcohol*, b. p. 130—135°/40 mm. (decomp.), d_4^{20} 1·8788, n_D^{20} 1·5130, and *tri-iodo*-tert.-*amyl alcohol*, d_4^{20} 2·1438, n_D^{20} 1·5680. The products are yellow, pungent liquids, which produce a numbing sensation when placed on the tongue. The first two, but not the last, are fairly stable in the dark, and they are all less stable than the corresponding trihalogeno-*tert.*-butyl alcohols. F. G. W.

Comparison of Hydrogen Ion and Enzyme Catalysis of certain Sugars and Glucosides. R. Kuhn and H. Sobotka (*Z. physikal. Chem.*, 1924, **109**, 65—76).—In the enzymic hydrolysis of sugar derivatives an enzyme–sugar compound is formed as an intermediate product (cf. Kuhn, A., 1923, i, 1033). It has been

found (unpublished work) that the rates of enzyme hydrolysis of α-phenylglucoside, α-methylglucoside, and maltose vary as the corresponding rates of acid hydrolysis, and similar relations hold for raffinose and sucrose, but not for helicin, salicin, and β-methyl- and β-phenyl-glucosides. Various reasons are suggested to account for the difference, including the possibility that it may be due to the large differences between the acid dissociation constants of the different glucosides. Experiments have therefore been made to determine the influence of the hydrogen-ion concentration on the dissociation constant of the emulsin–salicin compound in the hydrolysis of salicin by emulsin. The maximum activity of the enzyme is obtained at p_H 4·4, and falls to half value at p_H 6·8. The concentration of salicin at which the activity is half the maximum, increases from 0·035*N* for p_H 4·4 to 0·047*N* for p_H 6·8. According to Michaelis and Rothstein (A., 1920, i, 896), it should, on the contrary, fall to half. The salicin–emulsin compound is to be regarded as half dissociated at these concentrations of salicin, that is, the dissociation constants are 0·035 at p_H 4·4 and 0·047 at p_H 6·8.

The acid dissociation constants of a number of sugars and glucosides have also been determined, and several differ to a rather large extent from those found by Michaelis and Rona (A., 1913, ii, 379).

M. S. B.

Stepwise Oxidation of Dextrose. M. Hönig and F. Tempus (*Ber.*, 1924, **57**, [*B*], 787—791).—Cautious oxidation of dextrose by means of cold barium hypobromite, in presence of a slight excess of barium hydroxide, effects a stepwise oxidation in which the chief products are gluconic acid, β-ketogluconic acid, and arabonic acid, using 1, 2, or 3 equivalents of oxygen, respectively. Further oxidation affords a complex mixture of various substances such as arabonic, saccharic, tartaric, formic, and acetic acids. The constitution of ketogluconic acid was shown by its degradation by carboxylase to *d*-arabinose. Ketogluconic acid was identified by its *calcium* salt, [α] −9·56°, and *osazone*, bright yellow needles, m. p. 174°.

F. A. M.

Polysaccharides. XXVI. Cleavage of Lichenin into Dextrose. P. Karrer and M. Staub (*Helv. Chim. Acta*, 1924, **7**, 518—519).—The quantitative conversion of lichenin (reserve cellulose) into dextrose by lichenase (cf. A., 1923, i, 1182) has been confirmed by the preparation of the crystalline sugar in almost quantitative yield from the fermented lichenin solution.

E. H. R.

Acetone [*iso*Propylidene] Compounds of the Mercaptals of certain Monosaccharides. I. Acetone Compounds of *d*-Glucosedibenzylmercaptal. E. Pacsu (*Ber.*, 1924, **57**, [*B*], 849—853).—*d*-Glucosedibenzylmercaptal, $[\alpha]_D^{15}$ −98·37° in pyridine, m. p. 139° (Lawrence, A., 1896, i, 272, gives m. p. 133°), condenses with acetone to form a brown syrup which was separated by means of chloroform and light petroleum into the crystalline

monoacetone-d-*glucosedibenzylmercaptal*, m. p. 94°, $[\alpha]_D^{15}$ −16·44° (in tetrachloroethane), and the yellow, syrupy *diacetone*-d-*glucosedibenzylmercaptal*, which was treated with *p*-toluenesulphonyl chloride in pyridine to give p-*toluenesulphonyldiacetone*-d-*glucosedibenzylmercaptal*, colourless needles, m. p. 114°, $[\alpha]_D^{15}$ −51·89° (in tetrachloroethane). The crude mixture of *iso*propylidene dimercaptal was converted by methylation and subsequent hydrolysis of the product into *monomethyl*-d-*glucosedibenzylmercaptal*, colourless needles, m. p. 190—191°, $[\alpha]_D^{15}$ −109·02° in pyridine, and *trimethyl*-d-*glucosedibenzylmercaptal*, $C_6H_5(OH)_4(OMe)(S{\cdot}CH_2Ph)_2$, hexagonal platelets, m. p. 73—74°, $[\alpha]_D^{15}$ −63·12° in pyridine. F. A. M.

Synthetic Action of α-*d*-Mannosidase in the Presence of some Monohydric Alcohols. H. Hérissey and J. Cheymol (*Bull. Soc. Chim. biol.*, 1924, **6**, 186—189).—The action on mannose of α-*d*-mannosidase from lucerne grains (A., 1913, i, 497) in the presence of ethyl, propyl, *iso*propyl, or *n*-butyl alcohol results in the synthesis of the corresponding α-mannoside. J. P.

Isolation of Sucrose from Mixtures of Dextrose, Lævulose, and Sucrose. S. Komatsu and M. Tanimura (*Mem. Coll. Sci., Kyōtō*, 1924, **7**, 161—163).—Sucrose was isolated in the crystalline state from mixtures with lævulose and dextrose after transforming the reducing sugars into the sugar acids by oxidation with yellow mercuric oxide in the presence of calcium carbonate. The solution was kept neutral in order to reduce the hydrolysis of the sucrose. The sucrose was then crystallised from glacial acetic acid. H. C. R.

Oxidation of Lævulose in Phosphate Solutions. O. Warburg and M. Yabusoe (*Biochem. Z.*, 1924, **146**, 380—386).—In the presence of phosphates lævulose, but not dextrose, is oxidised by molecular oxygen with the formation of ⅓ mol. of carbon dioxide per mol. of oxygen absorbed. The rate of oxidation, which is most rapid during the first few hours, then slowly decreases; it increases with increasing p_H, and with the phosphate and lævulose concentration, other factors being kept constant. The phosphate cannot be replaced by other salts, and its action is regarded as specific. J. P.

Reaction of Acetohalogen-sugars with Tertiary Bases. P. Karrer, A. Widmer, and J. Staub (*Helv. Chim. Acta*, 1924, **7**, 519—527; cf. A., 1921, i, 766).—By the action of trimethylamine on acetobromocellobiose a substance is obtained having the composition $C_{12}H_{14}O_{10}Ac_6$, long, white needles, m. p. 206°, $[\alpha]_D$ −11·3°, to which the name *cellal acetate* is given. It cannot be hexa-acetylanhydrocellobiose, since it reduces Fehling's solution (in presence of alcohol or pyridine as solvent) and is quite stable to acids. By vigorous treatment with acetic anhydride and sodium acetate, it gives octa-acetylcellobiose. Unlike the latter compound, it is not converted into aceto-αζ-dibromoglucose by phosphorus pentabromide.

The tetra-acetylglucosidopyridinium bromide of Fischer and Raske is hydrolysed by dilute hydrobromic acid to *glucosidopyridinium bromide*, m. p. 179°, $[\alpha]_D$ +41·4°; the corresponding *chloride* has m. p. 177°, $[\alpha]_D$ +49·2°, the *iodide*, m. p. 183°, and the *perchlorate*, m. p. 170°. The fact that the pyridinium salt does not give lævoglucosan when hydrolysed with alkali, and that the acetyl compound has a negative rotation, suggests that the pyridinium salt has an α-configuration, whilst tetra-acetylglucosidotrimethylammonium salts (A., 1921, i, 766) have the β-configuration.

When ζ-bromotriacetyl-β-methylglucoside is heated with trimethylamine, *methylglucosidotrimethylammonium bromide*, white crystals which darken at 240°, m. p. 263—266° (decomp.), is obtained; the *chloride* has m. p. 274—275° (decomp.); *perchlorate*, broad needles, m. p. 125°; *picrate*, microcrystalline; *chloroaurate*, m. p. 136°. Extensive decomposition occurs when the salts are heated with alkali. E. H. R.

Absorptive Power of Starch for Gases and its Action on Magnesium Alkyl Derivatives. D. Costa (*Gazzetta*, 1924, **54**, 207—211).—The action of magnesium ethyl bromide on starch in ethereal solution and in complete absence of moisture (cf. A., 1923, i, 186) yields a grey, granular *compound*, $C_6H_9O_5 \cdot MgBr,Et_2O$.

Under similar conditions, starch absorbs about twice as much hydrogen chloride (above 18·55%) as does cellulose (cf. Oddo, A., 1920, i, 16) and undergoes transformation into a black substance completely soluble in water. Ammonia and sulphur dioxide also are absorbed by starch in the proportion of approximately 1 mol. per $C_6H_{10}O_5$, the starch undergoing no apparent change. Starch absorbs about 0·675% (or 0·065%) of its weight of carbon dioxide (or oxygen). T. H. P.

Starch. IX. Constitution of the Polyamyloses. H. Pringsheim and J. Leibowitz (*Ber.*, 1924, **57**, [*B*], 884—887; cf. A., 1923, i, 899).—By treatment of α-tetra-amylose or β-hexa-amylose with cold concentrated hydrochloric acid according to the method of A. and J. Pictet (A., 1923, i, 755) the authors have obtained a new disaccharide, termed *amylobiose*, $C_{12}H_{22}O_{11}$, which retains in its molecule the second bond of the glucose portion of diamylose, contrary to the views of Karrer and co-workers (A., 1922, i, 435). It is a pure white powder, $[\alpha]_D^{20}$ +138° in water (*osazone*, m. p. 189°). Amylobiose remained unattacked by maltase or emulsin, but was fermented by amylase; it is suggested that amylobiose is a glucosido-γ-glucose. F. A. M.

Starch. X. Different Structures of the Two Constituents of Starch. H. Pringsheim and K. Wolfsohn (*Ber.*, 1924, **57**, [*B*], 887—891; cf. A., 1923, i, 899, and preceding abstract).—The view of Pringsheim and Goldstein (A., 1923, i, 899) that the content- and integument-substances of the starch granule contain respectively a disaccharide and a trisaccharide has now been confirmed directly. Starch paste was separated into amylose and amylopectin, by the method of Ling and Nanji (T., 1923, **123**,

2666) and the two substances were depolymerised separately by acetylation (cf. Pringsheim and Eissler, A., 1913, i, 1156) and by heating to 200—210° in glycerol (cf. Pictet and Jahn, A., 1922, i, 987), with the addition of a small quantity of phosphoric acid. Acetylation of amylopectin with acetic anhydride and sulphuric acid gave an *acetate*, $C_{36}H_{48}O_{24}$, $[\alpha]_D^{20}$+143·6—144·2° in tetrachloroethane, whilst the *acetate* of *amylose*, $C_{24}H_{32}O_{16}$, had $[\alpha]_D^{20}$+142·4—142·8° in tetrachloroethane. Depolymerisation of amylopectin in glycerol gave a *trihexosan*, $C_{18}H_{30}O_{15}$, $[\alpha]_D^{20}$+165·2—167·5° in water, whilst amylose gave a dihexosan, $C_{12}H_{20}O_{10}$, $[\alpha]_D^{20}$+153·9—154·8° in water. The product obtained by Pictet and Jahn (*loc. cit.*) of $[\alpha]_D$ +162·2° was therefore a mixture of trihexosan and dihexosan.

F. A. M.

Behaviour of Cellulose and Lignin during Decay. F. Fischer (*Brennstoff-Chem.*, 1924, **5**, 132—133).—The work of Bray and Andrews (*Ind. Eng. Chem.*, 1924, **16**, 137) on the chemical processes during the bacterial decay of wood is cited in support of the author's hypothesis that the origin of coal is not principally the cellulose of dead vegetation but the lignin. Those authors showed that in the space of three years the cellulose calculated on the original wood had decreased down to 6·05%, whereas the lignin had practically resisted. Schwalbe's experiments whereby he prepared a substance resembling coal by the action of powerful dehydrating agents on cellulose are not held to be valid in determining the origin of coal because the conditions were so different from those prevailing in nature. It is far more probable that dead vegetation would be rapidly attacked by bacterial decay, with consequent destruction of the cellulose, than that it should be preserved and converted into coal by the accidental occurrence of powerful dehydrating conditions.

J. F. B.

Conversion of Ligneous Plant Substances into Coal. II. Chemical Composition and Properties of Coal-like Substances from Cellulose. C. G. Schwalbe and R. Schepp (*Ber.*, 1924, **57**, [*B*], 881—883; cf. this vol., i, 377).—Analytical figures are given for the composition of the coal-like substances obtained by heating wood-cellulose with concentrated solutions of salts during various periods. The artificial product appears to be more closely related to the lignites than to ordinary coal or to the humic acids, which was shown by analysis and by the behaviour both with alkalis and with nitric acid; there are, however, also very distinct differences in general behaviour between lignite and the artificial coal.

F. A. M.

Isomorphism of the Amides and Substituted Amides of Dichloro- and Chloroiodo-acetic Acids, and of Chlorobromo- and Chloroiodo-acetic Acids. [Miss] P. V. McKie (*J. Chem. Soc.*, 1924, **125**, 1075—1079).—The fusion mixtures of corresponding pairs of the amides and substituted amides of dichloro- and chloroiodo- and of chlorobromo- and chloroiodo-acetic acids show isomorphism (cf. T., 1923, **123**, 2213). In the corresponding series of

derivatives of dichloro- and chlorobromo-acetic acids the melting-point curve approximates to a straight line joining the melting points of the two components of each system, whereas the curves of pairs of derivatives of chlorobromo- and chloroiodo-acetic acids diverge from the straight line, the effect being very marked with derivatives of dichloro- and chloroiodo-acetic acids. The following compounds were prepared by methods similar to those previously employed (*loc. cit.*): *Chloroiodoacetomethylamide*, m. p. 117·5°; *chloroiodoacetoethylamide*, m. p. 79·4°; *chloroiodoacetobenzylamide*, m. p. 120·5°; *chloroiodoacetomethylanilide*, m. p. 88·0°; *chloroiodoacetoethylanilide*, m. p. 92·3°. C. J. S.

Alkylchloromalonamides. Influence of Homology on Taste. A. W. Dox and B. Houston (*J. Amer. Chem. Soc.*, 1924, **46**, 1278—1281).—Ethylchloromalonamide was obtained by the action of sulphuryl chloride on ethylmalonamide. Dichloromalonamide and the following alkylchloromalonamides were prepared by the action of chlorine on the appropriate malonamides in glacial acetic acid solution. *Methyl-*, m. p. 224—225°; *ethyl-*, m. p. 135°; n-*propyl-*, m. p. 150°; n-*butyl-*, m. p. 136°; iso*butyl-*, m. p. 132°; iso*amyl-*, m. p. 157°; n-*hexyl-*, m. p. 130°; and *benzylchloro-malonamide*, m. p. 183—185°. *iso*Propylmalonamide could not be chlorinated directly, and iso*propylchloromalonamide*, m. p. 177°, was obtained by the action of ammonia on *methyl* iso*propylchloromalonate*, a colourless oil, b. p. 110—112°/37 mm., 221—222°/757 mm., prepared by the chlorination of methyl *iso*propylmalonate. All the *n*-alkylchloroamides, as well as mono- and di-chloromalonamides, are sweeter than sucrose, the *n*-butyl derivative being at the same time bitter. The *iso*alkyl derivatives are bitter. Constant differences in sweetness between succeeding members of the series could not be established. F. G. W.

Derivatives of Semioxamazide. II. F. J. Wilson and E. C. Pickering (*J. Chem. Soc.*, 1924, **125**, 1152—1156).—In addition to the ketonic semioxamazones previously described (T., 1923, **123**, 394) others have been obtained by the same method. *Methyl* n-*hexyl ketone semioxamazone*, $C_6H_{13}\cdot CMe{:}N\cdot NH\cdot CO\cdot CO\cdot NH_2$, forms small, colourless needles, m. p. 115—116°. *Benzil monosemioxamazone*, long, colourless prisms, m. p. 181—182°. *Benzil disemioxamazone* is a white powder, m. p. 275—278° (decomp.). *Dibenzyl ketone semioxamazone* is dimorphic, colourless prisms, m. p. 195—196°, being deposited from alcohol above 40°, whilst at temperatures below this, and from more dilute solutions, it crystallises in colourless needles, m. p. 187—189°.

Benzylamine and semioxamazide interact on heating to form *s*-dibenzyloxamide hydrazone, hydrazine, and ammonia. Benzylamine and acetophenone semioxamazone, when heated at 150°, gave *s*-dibenzyloxamide, methylphenylketazine, m. p. 129—130°, hydrazine, and ammonia. Benzylamine and dibenzyl ketone semioxamazone react similarly to give *s*-dibenzyloxamide and *dibenzylketazine*, m. p. 95—96°, which has also been synthesised by heating dibenzyl ketone and hydrazine hydrate in a sealed tube at

100°. By the interaction of piperidine and acetophenone semioxamazone there results *acetophenone piperidino-oxalylhydrazone*, a white, microcrystalline powder, m. p. 174—175°, which is hydrolysed to *piperidino-oxalylhydrazine*, colourless, transparent plates, m. p. 77—79° (*hydrochloride*, m. p. 180°; *benzylidene* derivative, m. p. 201—202°). C. J. S.

Preparation and Hydrolysis of Substituted Cyanamides: Di-*n*-butylcyanamide and Diallylcyanamide. E. B. VLIET (*J. Amer. Chem. Soc.*, 1924, **46**, 1305—1308).—*Di*-n-*butylcyanamide*, a clear, slightly viscous liquid, b. p. 147—151°/35 mm., 187—191°/190 mm., and *diallylcyanamide*, a colourless liquid, b. p. 105—110°/18 mm., 140—145°/90 mm., are obtained by the action of *n*-butyl and allyl bromides, respectively, on a solution of sodium cyanamide obtained by the action of cold sodium hydroxide on an aqueous suspension of commercial calcium cyanamide, the reaction being facilitated by the addition of alcohol. The above cyanamides are hydrolysed to di-*n*-butylamine and diallylamine on boiling with 25% sulphuric acid. F. G. W.

Production of Thiocyanogen by Electrolysis of Alkali Thiocyanates. H. KERSTEIN and R. HOFFMANN (*Ber.*, 1924, **57**, [*B*], 491—496).—Thiocyanogen, first obtained by Söderbäck (A., 1920, i, 219) by the action of bromine on a suspension of silver thiocyanate in carbon disulphide, can be obtained by the electrolysis of alkali thiocyanates in aqueous or alcoholic solutions, using a platinum-gauze anode and a silver cathode. By evaporating the methyl-alcoholic solution at very low pressure, the thiocyanogen was left as a viscous oil which became solid at −70° and gradually crystallised. The thiocyanogen united with thiocyanates to form trithiocyanates, $M(SCN)_3$ (cf. tri-iodides), which behaved precisely like free thiocyanogen except for their smaller sensitiveness towards water. F. A. M.

Reduction of Pyruvylhydroxamic Acid Phenylhydrazone. V. C. GASTALDI (*Gazzetta*, 1924, **54**, 212—213).—Reduction of pyruvylhydroxamic acid phenylhydrazone by means of sodium amalgam at 0° (cf. A., 1923, i, 1236) proceeds in accordance with the scheme: $NHPh{\cdot}N{:}CMe{\cdot}CO{\cdot}NH{\cdot}OH \xrightarrow[-O]{} NHPh{\cdot}N{:}CMe{\cdot}CO{\cdot}NH_2 \xrightarrow[+2H]{} NHPh{\cdot}NH{\cdot}CHMe{\cdot}CO{\cdot}NH_2 \xrightarrow[+H_2O]{} NHPh{\cdot}NH{\cdot}CHMe{\cdot}CO_2H + NH_3$. The intermediate products obtained are thus: (1) α(β-phenylhydrazido)-propionamide, $NHPh{\cdot}NH{\cdot}CHMe{\cdot}CO{\cdot}NH_2$, m. p. 124° (cf. Reissert, A., 1884, 1152; Miller and Plöchl, A., 1892, 1196), and (2) *pyruvamide phenylhydrazone*, $NHPh{\cdot}N{:}CMe{\cdot}CO{\cdot}NH_2$, which crystallises in nacreous, white laminæ, m. p. 144°, and may be obtained also by dehydrogenating compound (1) by treatment with the alkaline tartrate solution used in preparing Fehling's solution. T. H. P.

Derivatives of Pyruvylhydroxamic Acid. VI. C. GASTALDI (*Gazzetta*, 1924, **54**, 214—220).—Pyruvylhydroxamic acid phenyl-

hydrazone and its acetyl derivative, prepared as described by Pickard (T., 1902, **81**, 1573), melt at 178—179° and 142°, respectively, not at 148° and 113°, as stated by this author. Further, the oxime of this acid has m. p. 161° and not 143° as given by Whiteley (T., 1900, **77**, 1046).

Pyruvylhydroxamic acid semicarbazone, $NH_2{\cdot}CO{\cdot}NH{\cdot}N{:}CMe{\cdot}CO{\cdot}NH{\cdot}OH,H_2O$ or $NH_2{\cdot}CO{\cdot}NH{\cdot}N{:}CMe{\cdot}C(OH){:}NOH,H_2O$, colourless needles, m. p. 200° (decomp.), gives a deep violet-red coloration with ferric chloride in aqueous solution; its *acetyl* derivative forms colourless prisms, m. p. 170° (decomp.). The *thiosemicarbazone*, $3C_4H_8O_2N_4S,2H_2O$, m. p. 185° (decomp.), forms a silver mirror when heated with ammoniacal silver nitrate. The *β-naphthylhydrazone*, $C_{13}H_{13}O_2N_3$, forms lustrous, orange laminæ or slender needles, m. p. 182° (decomp.), dissolves in concentrated sulphuric acid to a deep yellow solution, and in alcoholic solution gives a dark green coloration with aqueous ferric chloride; its *sodium* salt forms chestnut-red prisms and explodes violently when heated, and its *acetyl* derivative crystallises in orange prisms, m. p. 147—148° (decomp.), and on fusion is converted into *5-hydroxy-1-β-naphthyl-3-methyl-1 : 2 : 4-triazole*, yellowish-brown prisms, m. p. 199°.

1-β-Naphthyl-3 : 5-dimethyl-1 : 2 : 4-triazole, $C_{14}H_{13}N_3$, obtained when pyruvylhydroxamic acid β-naphthylhydrazone is fused with acetic anhydride, separates in yellow prisms, m. p. 105—106°; its *hydrochloride*, prisms, has m. p. 257°. T. H. P.

Conversion of *n*-Butane-αββ-tricarboxylic Acid into its Triazide and into Aminomethyl Ethyl Ketone. T. Curtius and R. Gund (*J. pr. Chem.*, 1924, [ii], **107**, 177—192).—Ethyl butane-αββ-tricarboxylate (cf. Bischoff, A., 1890, 742), b. p. 153—155°/9 mm., treated with hydrazine hydrate gives the *trihydrazide*, $C_2H_5{\cdot}C(CO{\cdot}NH{\cdot}NH_2)_2{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$, needles, m. p. 167°. This is not converted into a hydrazihydrazide by the action of iodine but only into the original acid and hydrazine dihydriodide. The *tribenzylidene* compound, m. p. 244° (decomp.); *derivatives* with salicylaldehyde, m. p. 212°; *p*-tolualdehyde, m. p. 249° (decomp.); *o*-chlorobenzaldehyde, m. p. 262°; *o*-nitrobenzaldehyde, m. p. 303°; acetone, m. p. 156°; and benzophenone, m. p. 162°; the *triacetyl* compound, m. p. 222°; *tribenzoyl* compound, m. p. 236°; *hydrochloride*, m. p. 185°, and *picrate*, m. p. 185°, are described. When treated as hydrochloride with sodium nitrite the trihydrazide is converted into the *triazide*, an explosive lachrymatory oil, decomposing even in ethereal solution at 0°. Treated with aniline in the cold, this gives *butane-αββ-tricarboxyanilide*, needles, m. p. 217°; the corresponding *tri-p-toluidide* forms prisms, m. p. 186°. With alcohol, the *urethane*, $CEt(NH{\cdot}CO_2Et)_2{\cdot}CH_2{\cdot}NH{\cdot}CO_2Et$, an oil, is formed, and when this substance is hydrolysed with hydrochloric acid at 80°, the hydrochloride of α-amino-β-ketobutane (Kolshorn, A., 1904, i, 675) is produced. When the triazide is decomposed by heating its solution in benzene the *carbimide*, $C_2H_5{\cdot}C(NCO)_2{\cdot}CH_2{\cdot}NCO$,

is formed. This substance, an oil, interacts with aniline to yield *butenyltri-phenylcarbamide*,

$$CEt(NH\cdot CO\cdot NHPh)_2\cdot CH_2\cdot NH\cdot CO\cdot NHPh,$$

white crystals soon turning yellow, m. p. 225°, which may be hydrolysed giving the above aminoketone, aniline, carbon dioxide, and ammonia. W. A. S.

Rubidium and Cæsium Creatinine Picrates. I. GREENWALD and J. GROSS (*J. Biol. Chem.*, 1924, **59**, 613—614).—The double picrates of creatinine with rubidium and with cæsium, m. p. 256—257° and 255°, respectively, were prepared by mixing hot solutions of creatinine, picric acid, and the sulphate or chloride of the metal. C. R. H.

Ultra-violet Absorption Spectrum of Naphthalene Vapour. V. HENRI and H. DE LÁSZLÓ.—(See ii, 367.)

Methylnaphthalenes. I. α-Methylnaphthalenesulphonic Acids. K. ELBS and B. CHRIST (*J. pr. Chem.*, 1923, [ii], **106**, 17—24).—α-Methylnaphthalene (b. p. 241°, picrate, m. p. 141°) was converted by the action of sulphuric acid at the ordinary temperature into *1-methylnaphthalene-4-sulphonic acid*, which was separated by means of its barium salt, a small amount of an isomeric barium salt being found in the mother-liquors. The free acid is deliquescent, exceedingly soluble in water, and readily soluble in concentrated sulphuric acid. The *barium* salt ($+1H_2O$) crystallises in colourless plates, the *copper* salt ($+4H_2O$) in small, pale green crystals. Attempts to oxidise the methyl group to the carboxyl group by means of potassium permanganate under varying conditions were unsuccessful. The *sulphochloride*, $C_{10}H_6Me\cdot SO_2Cl$, m. p. 81°; *sulphonamide*, m. p. 174°; *sulphonhydrazide*, m. p. 124—125° (decomp.); *acetyl* derivative of the hydrazide, m. p. 220—222° (decomp.); *sulphanilide*, m. p. 158°; the *methyl* ester, m. p. 107°, and the *ethyl* ester, m. p. 98°, are described. *1-Methylnaphthalene-4-sulphinic acid*, obtained by reduction of the sulphochloride with zinc dust, crystallises in needles, m. p. 114—115°; the *sodium* salt ($+3H_2O$) and the *copper* salt are described. *4-Thiol-1-methylnaphthalene*, $C_{10}H_6Me\cdot SH$, results in an impure form on reduction of the sulphochloride with iron turnings and hydrochloric acid; it is a yellow oil distilling between 168° and 178°/25 mm. The *lead* and *mercury mercaptides* form yellow precipitates. *1 : 1′-Dimethyldinaphthyl 4 : 4′-disulphide*, $C_{10}H_6Me\cdot S\cdot S\cdot C_{10}H_6Me$, obtained by the action of alcoholic ammonia on the thionaphthol, is a colourless, crystalline solid, m. p. 114°. 4-Methyl-α-naphthol is obtained from the acid by the ordinary method. F. G. P.

Course of Reaction in the Gattermann Synthesis of Diphenyl and the Formation of Para Chains of Benzene Rings. O. GERNGROSS, L. SCHACHNOW, and R. JONAS (*Ber.*, 1924, **57**, [*B*], 747—750).—In the Gattermann synthesis of diphenyl (A., 1890, 970) a small amount of *p*-phenyldiphenyl is produced simultaneously. The yield of diphenyl diminishes with decrease in alcohol concen-

tration, owing to the diminished solubility of the intermediately formed benzene, which is thus prevented from reacting with fresh diazonium salt. When diphenyldiazonium sulphate was treated with benzene and copper powder in a mixture of acetic, formic, and sulphuric acids, diphenyl (1 g.), *p*-phenyldiphenyl (0·3 g.) and *pp'*-diphenyldiphenyl (0·02 g.), were obtained. The mechanism of the reaction is therefore $C_6H_4Ph{\cdot}N_2Cl+C_6H_6=Ph{\cdot}C_6H_4{\cdot}Ph+N_2+HCl$. By a modification of the usual Gattermann synthesis from aniline (31 g.), diphenyl (4·2 g.), *p*-phenyldiphenyl (1·8 g.), *pp'*-diphenyldiphenyl (1·0 g.), and didiphenylylbenzene (0·11 g.) were isolated. (Cf. also *infra*.) F. A. M.

Studies in the Anthracene Series. IX. E. de B. Barnett and J. W. Cook (*J. Chem. Soc.*, 1924, **125**, 1084—1087).—The reaction between anthracene and bromine is reversible (cf. T., 1923, **123**, 1994), and by treatment of the anthracene dibromide with dilute hydriodic acid or compounds such as phenol which readily take up bromine, anthracene is regenerated. By the decomposition of anthracene dibromide on warming, dibromoanthracene is formed in addition to 9-bromoanthracene, but the formation of the dibromo compound is inhibited by phenol. The action of chlorine on 9-bromoanthracene is more rapid than on anthracene, but the only product isolated was 9-*chloro*-10-*bromoanthracene*, lemon-yellow needles, m. p. 207°. The same product was obtained by the action of sulphuryl chloride. On treatment with nitric acid in glacial acetic acid, 9-bromoanthracene yields 9 : 10-dibromoanthracene, 9-nitroanthrone, and probably a little bromonitroanthracene. The mechanism of the reaction is discussed. R. B.

Reduction of Organic Halogen Compounds. VII. 3-Phenyl-1-diphenylmethylene-indene. K. Brand and L. W. Berlin (*Ber.*, 1924, **57**, [*B*], 846—847; cf. A., 1921, i, 783).—The constitution of the hydrocarbon, m. p. 207—208°, obtained from βγ-dichloro-ααδδ-tetraphenyl-Δ^{β}-butene has now been proved by its synthesis from 3-phenylindene and benzophenone in presence of sodium ethoxide, and the formula previously ascribed, $C_6H_4<^{\text{---CPh}}_{\text{C(:CPh}_2)}>CH$, is therefore correct. The synthesis also confirms the structure assigned to the substance $C_{32}H_{28}O_4$, m. p. 173° (A., 1921, i, 787), obtained by the reduction of βγ-dichloro-ααδδ-tetra-*p*-anisyl-Δ^{β}-butene, and proves that compounds of the tetra-arylbutane series are easily converted into indene derivatives. R. B.

A Para Linking of the Benzene Ring; Extension of the Gattermann Diphenyl Synthesis and Quinquephenyl [Didiphenylylbenzene], a Straight Chain of Five Benzene Nuclei. O. Gerngross and M. Dunkel (*Ber.*, 1924, **57**, [*B*], 739—746).—Aniline was diazotised in a mixture of concentrated sulphuric acid and glacial acetic acid, by amyl nitrite; glacial formic acid was added and then copper powder by degrees at 0—2°. On steam

distillation diphenyl was obtained in the distillate (10·3%); 24·8% of the non-volatile, insoluble residue sublimed in a vacuum, at 135° to 400°/30 mm. This product was separated into *p*-phenyldiphenyl, *pp'*-diphenyldiphenyl, and didiphenylylbenzene,

$$C_6H_4Ph{\cdot}C_6H_4{\cdot}C_6H_4Ph.$$

The *p*-phenyldiphenyl had m. p. 209·5°, as compared with 207·5° when made from benzenediazonium chloride diphenyl, and aluminium chloride, and its other properties differ slightly from those given in the literature. The *pp'*-diphenyldiphenyl had m. p. 320°, in agreement with Ullmann's figure (A., 1904, i, 725). *Didiphenylylbenzene* is a faintly yellow substance, m. p. 388·5°, very sparingly soluble in all organic solvents; it was also prepared by Pummerer's method (A., 1922, i, 24, 1196) from *p*-iodophenyldiphenyl, *p*-iododiphenyl, and silver powder. F. A. M.

Specific Heats of certain Organic Liquids at Elevated Temperatures. J. W. Williams and F. Daniels.—(See ii, 450.)

Equilibrium of the System Ferric Chloride–Aniline Hydrochloride–Hydrogen Chloride–Water at 25°. Y. Osaka, G. Shima, and R. Yoshida (*Mem. Coll. Sci. Kyōtō*, 1924, **7**, 69—76).—Investigation of this system from the point of view of the phase theory indicates the existence of the two double salts :

$$FeCl_3,6(NH_2Ph,HCl),$$

in yellowish crystals, and $FeCl_3,2(NH_2Ph,HCl)$ in bluish-green, acicular crystals. The two hydrated salts obtained by McKenzie (A., 1913, i, 1321) were not formed under the conditions employed. T. H. P.

The Imino Residue. K. F. Schmidt (*Ber.*, 1924, **57**, [*B*], 704—706).—Azoimide is converted by concentrated sulphuric acid partly into hydroxylamine, some oxidation also occurring. At the atmospheric temperature, azoimide dissolved in benzene is transformed by concentrated sulphuric acid mainly into hydrazine, hydroxylamine and aniline being produced in small amount; at 60°, the main product is aniline sulphate, very little hydrazine being formed. Addition of carbonyl derivatives greatly accelerates the decomposition of azoimide by concentrated sulphuric acid and causes the immediate withdrawal of the liberated radical, NH, from the oxidising action of the acid, so that it is possible to convert N_3H quantitatively into NH. Ketones yield acid amides, $R{\cdot}CO{\cdot}R + NH \longrightarrow R{\cdot}CO{\cdot}NHR$, whereas aldehydes give nitriles or substituted formamides. α-Ketonic acids are converted into α-amino acids, the yields being 80—98% of the theoretical (glycine, α-aminobutyric acid, leucine, *α-amino-δ-methylhexoic acid*, phenylalanine, aspartic acid, and *α-aminodibenzylacetic acid* are thus prepared). *cyclo*Hexanone gives ε-leucyl-lactam, $\begin{matrix}CH_2{\cdot}CH_2{\cdot}CH_2\\ |\\ CH_2{-}CH_2{-}CO\end{matrix}\!>\!NH$, or with an excess of azoimide the tetrazole, $N\!<\!\begin{matrix}N{\cdot}N\\ |\\ N{:}C\end{matrix}\!>\![CH_2]_5$. Acyclic ketones likewise yield tetrazoles with an excess of azoimide, acetone

giving the compound $CMe<\begin{matrix}N—N\\ NMe\cdot N\end{matrix}$, whereas benzophenone gives 5-anilino-1-phenyl-1 : 2-dihydrotetrazole. H. W.

Nitrogen Chlorides derived from Nitro-substituted Acetanilides. F. D. CHATTAWAY and H. J. DOWDEN (*J. Chem. Soc.*, 1924, **125**, 1195—1197).—*N*-Chloro derivatives of polynitroacetanilides are not transformed into chloronitroacetanilides, but are hydrolysed and decomposed, or the original nitroacetanilide is regenerated. The transformation of *N*-chloro-2- and -3-nitroacet-*p*-toluidides is also inhibited by the presence of the nitro group. N-*Chloro*-2 : 4-*dinitroacetanilide*, m. p. 54—55°, is obtained by the action of chlorine on 2 : 4-dinitroacetanilide in acetic acid solution. 6-Chloro-2 : 4-dinitroacetanilide, m. p. 221°, on treatment with hypochlorous acid in chloroform yields N : 6-*dichloro*-2 : 4-*dinitroacetanilide*, m. p. 68·5°. 2 : 4 : 6-Trinitroacetanilide is not attacked by chlorine in acetic acid solution, but in sodium hydroxide solution it yields N-*chloro*-2 : 4 : 6-*trinitroacetanilide*, m. p. 127·5°. N-*Chloro*-2-*nitroacet*-p-*toluidide*, m. p. 125—126°, is obtained by the action of hypochlorous acid on 2-nitroacet-*p*-toluidide in chloroform. N-*Chloro*-3-*nitroacet*-p-*toluidide*, m. p. 51·5°, is similarly prepared from the 3-nitrotoluidide. R. B.

Preparation of Anilides of Glycine. P. KARRER and W. T. HAEBLER (*Helv. Chim. Acta*, 1924, **7**, 534—536).—Glycineanilide is simply prepared by reducing Sandmeyer's oximinoacetanilide (A., 1919, i, 318) either electrolytically or with zinc dust and acetic acid. *Glycylanthranilic acid*, $CO_2H\cdot C_6H_4\cdot NH\cdot CO\cdot CH_2\cdot NH_2$, obtained by reduction of oximinoacetylanthranilic acid, has m. p. 233—234°; *sulphate*, white crystals. Glycyl-*p*-phenetidine (phenocoll) is obtained similarly from oximinoacetyl-*p*-phenetidine. E. H. R.

Naphthol AS [2-Hydroxy-3-naphthoanilide] Derivatives. M. BATTEGAY, C. LANGJAHR, and P. RETTIG (*Chim. et Ind.*, 1924, **11**, 453—455).—β-*Naphthaquinone*-1-*oxime*-3-*carboxyanilide*, obtained by the action of nitrous acid on Naphthol AS, forms red needles which decompose at 200° without melting, soluble in warm sodium hydroxide solution. The sodium compound, when treated with sodium hydrogen sulphite solution, yields a hydrogen sulphite compound which dyes cotton better than does the corresponding β-naphthol derivative. 1-*Amino*-2-*hydroxynaphthalene*-3-*carboxyanilide*, obtained by the reduction of the quinoneoxime, crystallises in fine needles, m. p. 180°. β-*Naphthaquinone*-3-*carboxyanilide*, brick-red crystals, m. p. 204°, yields a red solution in sulphuric acid. The *Meldola-blue*, prepared from Naphthol AS instead of β-naphthol, is insoluble in water but soluble in acetic acid; it dyes cotton a duller shade than does ordinary Meldola-blue. W. P. S.

Reactions of Tetryl [2 : 4 : 6-Trinitrophenylmethylnitroamine]. T. L. DAVIS and C. F. H. ALLEN (*J. Amer. Chem. Soc.*, 1924, **46**, 1063—1065).—Commercial samples of tetryl often contain occluded acid. When tetryl is heated with hexyl or *n*-butyl

alcohol, methylpicramide (picrylmethylamine) is formed in small quantities (cf. Mertens, A., 1886, 1022). Tetryl is not affected by prolonged boiling with dilute sulphuric acid, but with aqueous chromic acid it yields picric acid. In the presence of glacial acetic acid, tetryl is destroyed by chromic acid. It is rapidly dissolved by concentrated sulphuric acid at 100°, forming a red solution, and is reprecipitated on pouring this solution on to ice. If the solution is allowed to stand for some days and then poured on to ice, a gummy material is precipitated which dissolves in warm alcohol. The solution deposits 20% of the theoretical yield of picrylmethylamine. As picrylmethylamine yields tetryl on nitration, the reaction is reversible. [Cf. *B.*, 1924, 539.] A. C.

Colour Tests for Nitro Derivatives of Diphenylamine. T. L. Davis and A. A. Ashdown (*J. Amer. Chem. Soc.*, 1924, **46**, 1051—1054).—Such nitro derivatives as were likely to be found in smokeless powder which has been stored for some time, were prepared in a state of high purity (detailed methods are given), and their colour reactions with alcoholic solutions of sodium hydroxide, ammonia, and sodium cyanide, as well as with sulphuric acid, were examined under standardised conditions. The derivatives examined were *o*-, *m*-, and *p*-nitrodiphenylamine; 2 : 4-, 2 : 4′-, 4 : 4′-dinitro-; 2 : 4 : 6- and 2 : 4 : 4′-trinitro-; 2 : 4 : 2′ : 4′- and 2 : 4 : 6 : 4′-tetranitro-diphenylamines, together with diphenylnitrosoamine. The colours are compared according to the standard colour chart of Mulliken (" Identification of Pure Organic Compounds," Vol. I). An attempt to prepare *o*- and *p*-nitrodiphenylnitrosoamines by nitrating diphenylnitrosoamine in glacial acetic acid at 15° led to the formation of *p*-nitrosodiphenylamine (Fischer-Hepp rearrangement) and nitrodiphenylamines with nitro groups in the para-position. Derivatives with melting points higher than previously recorded were: 4 : 4′-dinitro-, 216—216·5°; 2 : 4′-dinitro-, 220—221·5°; and 2 : 4 : 2′ : 4′-tetranitro-diphenylamine, 201—201·5°. A. C.

Hydrindene. II. W. Borsche and G. John (*Ber.*, 1924, **57**, [*B*], 656—662; cf. Borsche and Pommer, A., 1921, i, 168).—5-Aminohydrindene, coarse needles, m. p. 37—38°, b. p. 247—249°/745 mm., is prepared by the action of phosphorus pentachloride on an ethereal solution of 5-acetylhydrindeneoxime or of bromine and sodium hydroxide solution on hydrindene-5-carboxyamide. When diazotised and coupled with β-naphthol or 5-hydroxyhydrindene, it yields *5′-hydrindeneazo-β-naphthol*, carmine-red leaflets, m. p. 156—157°, or *5′-hydrindene-4(?)-azo-5-hydroxyhydrindene*, brown needles, decomp. 175°.

5-Hydroxyhydrindene, m. p. 55°, is obtained in moderate yield from 5-aminohydrindene through the diazo compound, or more readily by fusing sodium hydrindene-5-sulphonate with sodium hydroxide at 280—290°; the corresponding *benzoate* forms colourless leaflets, m. p. 106—107°. The phenol couples with diazobenzene-*p*-sulphonic acid to give the orange-red *dye*,

$$C_{15}H_{12}O_4N_2SNa_2,$$

which is converted by sodium hyposulphite into 4(?)-amino-5-hydroxyhydrindene, m. p. 183—184°. 4 : 6-*Dinitro-5-hydroxyhydrindene* forms dark yellow leaflets or needles, m. p. 106—107°. 5-Hydroxyhydrindene is converted by bromine in glacial acetic acid solution into a colourless, crystalline substance, m. p. 40—41°, which loses hydrogen bromide when kept and passes into dibromo-5-hydroxyhydrindene, a colourless liquid (*benzoate*, leaflets, m. p. 139°).

5 : 5'-*Dihydrindyl ketone*, $C_{19}H_{18}O$, m. p. 117—118°, b. p. 245—250°/15 mm., is prepared from hydrindene-5-carboxylic chloride and hydrindene in the presence of carbon disulphide and aluminium chloride; the corresponding *oxime*, colourless needles, m. p. 173°, is isomerised to *hydrindene-5-carboxy-5'-hydrindylamide*, colourless needles, m. p. 173°, which is also obtained from hydrindene-5-carboxylic chloride and 5-aminohydrindene in the presence of pyridine.

5-Acetylhydrindene is converted successively into 4-*nitro*-5-*acetylhydrindene*, long, colourless needles, m. p. 51—52°, and 4-*nitro*-5-*acetylhydrindeneoxime*, colourless needles, m. p. 153—154°. The latter substance is transformed by successive treatment with phosphorus pentachloride and boiling hydrochloric acid (20%) into 4-*nitro*-5-*aminohydrindene*, orange-red needles, m. p. 92—93°. 4-*Nitro*-5-*benzoylaminohydrindene*, yellow crystals, m. p. 118—119°, is reduced by tin and fuming hydrochloric acid to 2-*phenyl*-4 : 5-*trimethylenebenziminazole*,

$$CH_2\langle\begin{matrix}CH_2\\CH_2\end{matrix}\rangle C_6H_2\langle\begin{matrix}-N\\NH\end{matrix}\rangle CPh,$$

b. p. about 280°/50 mm., m. p. 224—226° (decomp.). De-amination of 4-nitro-5-aminohydrindene in the usual manner gives 4-*nitrohydrindene*, a yellow liquid, which is reduced by iron and acetic acid to 4-*aminohydrindene*, a colourless liquid, b. p. 235°/754 mm. (*benzoyl* derivative, colourless leaflets, m. p. 135—136°; *azo* dye, obtained with β-naphthol, long, red needles, m. p. 141—142°). The base is also obtained by converting hydrindene-5-carboxylic acid into *nitrohydrindene-5-carboxylic acid*, m. p. about 140° (*amide*, colourless leaflets, decomp. 194°), reduction of the acid with tin and hydrochloric acid, and distillation of the crude amino-acid with potassium hydroxide. H. W.

Condensation of Cyclic Hexenes with Phenol. (Chemical Structure of Lignin.) W. Schrauth and K. Quasebarth (*Ber.*, 1924, **57**, [*B*], 854—858).—By condensing phenol with *cyclo*hexene in the presence of sulphuric and acetic acids (cf. Koenigs, A., 1891, i, 208, 571) *p-cyclo*hexylphenol, m. p. 130°, identical with that previously prepared from phenol and *cyclo*hexanol (A., 1923, i, 1084) is obtained. Condensation in the presence of concentrated hydrochloric acid gives the same product in poorer yield, with some *phenyl* cyclo*hexyl ether*, b. p. 125—127°/10 mm. In the absence of a catalyst, no condensation takes place. Similar results were obtained with the methyl*cyclo*hexenes. Condensation of phenol with the methyl*cyclo*hexenes prepared from 3-methyl-, 4-methyl-, 2-methyl-, and 1-methyl*cyclo*hexan-1-ol by Koenigs' method yielded in all cases p-*methyl*cyclo*hexylphenol*, felted needles, m. p. 112·5°,

whilst condensation with hydrochloric acid gave the same product in poorer yield, together with phenyl methyl*cyclo*hexyl ether, b. p. 129—130°/8·5 mm., d_4^{20} 0·9857. 1 : 3-Dimethyl-Δ^5-*cyclo*hexene and phenol in the presence of hydrochloric acid yielded *dimethylcyclohexylphenol*, fine needles, m. p. 68—73°, which gives the Liebermann reaction; octahydronaphthalene similarly yields *decahydronaphthylphenol*, fine needles, m. p. 127—128°. The alkali salts of these two phenols possess lathering properties. Similar products were obtained from pinene and limonene by condensation in the presence of hydrochloric acid, but the products could not be satisfactorily purified. All the condensation products are readily soluble in organic solvents.

The property of reacting in this way with phenol appears to be characteristic of the tetrahydrobenzene ring carrying side-chains or other ring systems, and in conjunction with the observation that lignin dissolves in phenol in the presence of traces of mineral acid, supports the view that lignin possesses an unsaturated hydroaromatic structure (cf. A., 1923, i, 443; ii, 502). R. B.

***cyclo*Hexyl Ether.** W. Schrauth and W. Wege (*Ber.*, 1924, 57, [*B*], 858).—Phenyl *cyclo*hexyl ether (cf. preceding abstract) in the presence of active nickel at 165—170° and under 10—15 atm., is readily converted into *cyclo*hexyl ether, $(C_6H_{11})_2O$, a mobile, colourless liquid, b. p. 239—240°, d_4^{20} 0·9241, identical with the product described by Willstätter and Hatt (A., 1912, i, 544). The discrepancy in the results obtained by Ipatiev (A., 1908, i, 342) is attributed to the high temperature and pressure employed by him (cf. A., 1923, i, 204). R. B.

Action of Chloropicrin on Phenol. S. Berlingozzi and P. Badolato (*Atti R. Accad. Lincei*, 1924, [v], **33**, i, 290—292).—The interaction of chloropicrin and phenol in presence of potassium hydroxide results in elimination of the nitro group, which effects oxidation and is itself reduced to ammonia. The principal products are *o*- and *p*-hydroxybenzaldehydes and the corresponding acids, and considerable quantities of pararosolic acid are formed, probably by condensation of the phenol with the hydroxybenzaldehyde.

T. H. P.

Tautomerism with Respect to Nitrosophenols. H. H. Hodgson (*J. Soc. Dyers and Col.*, 1924, **40**, 167—174).—No conclusion can be drawn from the work of previous investigators (cf. Bridge, A., 1894, i, 25) as to the existence of nitrosophenols as such, since the conditions employed in preparing derivatives all favour conversion into the quinone-oxime form before or during reaction. Similar causes are responsible for the poor yield and impure product obtained in nitrosating phenol in the usual way. If the nitrosation be carried out by dissolving the phenol in dilute sodium hydroxide solution, adding an excess of sodium nitrite, and then running dilute sulphuric acid in gradually, a clean product of m. p. 133° is obtained. When *m*-chlorophenol is

nitrosated in this way it gives 60% of the theoretical yield of m-*chloro*-p-*nitrosophenol*, needles, m. p. 135·8°, affording *m*-chloro-*p*-nitrophenol on oxidation. When boiled with dilute hydrochloric acid, the nitroso compound is converted into syn(?)-2-*chlorobenzoquinonemonoxime*, orange crystals, m. p. 172° (decomp.), and this is further converted into the *anti*(?) form, yellow needles, m. p. 178°, by solution in dilute sodium hydroxide and reprecipitation. A mixture of the two substances melts at 170·6°. The reverse change is brought about by treatment with hot dilute acid. Anti(?)-2-*chlorobenzoquinonemonoxime* may also be obtained directly from the true nitrosophenol by dissolving the latter in a saturated solution of sodium carbonate and reprecipitating it with acid. Alkali hydroxide causes further changes, impure products being obtained. W. A. S.

Reactions of Strongly Electropositive Metals with Organic Substances in Liquid Ammonia Solution. V. Syntheses of Oxygen and Sulphur Ethers and of Alkyl Derivatives of Ammono Acids. G. F. WHITE, A. B. MORRISON, and E. G. E. ANDERSON (*J. Amer. Chem. Soc.*, 1924, **46**, 961—968).—A number of organic compounds, containing hydroxyl, thiol, amino, or imino groups, which possess acidic character, react with the alkali metals or with alkali amides in liquid ammonia. The salts formed are more or less soluble in the liquid ammonia, and many of them react in that medium with organic halides and form compounds in which the hydrocarbon radical of the halide has replaced the metal atom of the salt. The latter reaction is often quantitative, particularly in cases where there is no action between the halide and liquid ammonia. The speed of the reaction depends largely on the solubility of the salt formed. The reactions approach the ionic type, being completed within 5 minutes at −33°. Methyl iodide reacts vigorously with liquid ammonia, producing tetramethylammonium iodide, and is therefore not suitable for these reactions. Ethyl iodide and benzyl chloride have only a slight action, whilst *n*-butyl bromide, ethylene bromide, and iodobenzene do not react at all. Aliphatic ethers were synthesised by dissolving an atomic proportion of potassium (or sodium) in liquid ammonia, adding a molecular proportion of an alcohol (when the alkoxide was partly or wholly precipitated) followed by the halide. The ether was isolated after distilling off the ammonia under water. Its yield depended largely on the solubility of the alkoxide. The yield of ethyl ether was 71% of theory, ethyl *n*-butyl ether 19%, benzyl ethyl ether 81%, benzyl ether 55%. The phenoxides of the alkali metals are more soluble in liquid ammonia and react readily with alkyl halides. Anisole was obtained in 42% yield by passing gaseous methyl chloride into a solution of sodium phenoxide in liquid ammonia. Phenetole was obtained in 59·5% yield, using ethyl bromide. A small amount of phenetole is obtained when ethyl iodide is allowed to stand with phenol in liquid ammonia in the absence of a metal. Phenyl *n*-butyl ether was obtained in 28% yield. Neither ethylene bromide nor chloride reacts with

sodium phenoxide to form diphenyl ethylene ether. α-Naphthol reacts with sodium in liquid ammonia, giving a clear solution, but no hydrogen is given off, the naphthol being partly reduced to tetrahydronaphthol. A mixture of the ethers of naphthol and tetrahydronaphthol was obtained on adding an alkyl halide. β-Naphthyl ethyl ether was obtained in this way using ethyl iodide; yield 61% of theory. Resorcinol and ethyl iodide gave small yields of the mono- and di-ethyl ethers. Thiophenols are more reactive, and evidence of the formation of an ammonium phenyl sulphide was obtained. Thiophenol added to ethyl bromide in liquid ammonia resulted in 76% of the theoretical yield of the thio-ether, the preparation of a metal compound being unnecessary. Phenyl *n*-propyl sulphide and diphenyl ethylene disulphide were prepared in 86 and 98% yields, respectively. Certain amino and imino compounds of acidic character form metallic amides which react with alkyl (not aryl) halides. Thus acetamide forms potassium acetamide which reacts with ethyl bromide to form acetethylamide (34% yield). Diphenylamine gives a soluble potassium compound which with ethyl bromide leads to a quantitative yield of diphenylethylamine. Acetethylanilide (40% yield) and ethylphthalimide (small yield) were similarly prepared. A. C.

o-Nitrotoluene-*p*-sulphon-*p*-anisidide and its Nitration Products. F. REVERDIN (*Helv. Chim. Acta*, 1924, **7**, 567—574).—The following nitro derivatives of *o*-nitrotoluene-*p*-sulphon-*p*-anisidide were prepared to investigate the formation by such compounds of molecular compounds and substitution products with aliphatic and aromatic amines. Nitration of *o*-nitrotoluene-*p*-sulphon-*p*-anisidide in acetic acid solution with nitric acid, *d* 1·38, at about 0° gives a high yield of o-*nitrotoluene*-p-*sulphon*-3-*nitro*-p-*anisidide*, lemon-yellow crystals, m. p. 135°. It gave no definite compounds with amines. Nitration of a paste of the anisidide with glacial acetic acid at 0°, using nitric acid *d* 1·51, gave as principal product o-*nitrotoluene*-p-*sulphon*-2 : 3-*dinitro*-p-*anisidide*, pale yellow, transparent prisms, m. p. 178—179°. This forms a *compound*, m. p. 158°, with ethylamine, and a particularly stable *compound* with diethylamine, $C_{14}H_{12}O_9N_4S,NHEt_2$, lemon-yellow needles, m. p. 194°. As a by-product of the second method of nitration there is formed o-*nitrotoluene*-p-*sulphon*-2 : 5-*dinitro*-p-*anisidide*, lemon-yellow needles, m. p. 152°. By further nitrating the above 3-nitro-*p*-anisidide, o-*nitrotoluene*-p-*sulphon*-3 : 5-*dinitro*-p-*anisidide* was obtained, pale yellow needles, m. p. 147°. By heating 2 : 3-dinitro-*p*-anisidide with nitric acid, *d* 1·4, at 70—80°, o-*nitrotoluene*-p-*sulphon*-2 : 3 : 5-*trinitro*-p-*anisidide* is formed, small, white prisms, m. p. 188—189°. This forms *compounds* with ethylamine, $C_{14}H_{11}O_{11}N_5S,NH_2Et$, orange prisms, m. p. indistinct, near 149°, and with diethylamine, $C_{14}H_{11}O_{11}N_5S,NHEt_2$, lemon-yellow prisms, m. p. about 168—169°. With aniline it forms a substitution *compound*, $C_{20}H_{17}O_9N_5S$, yellow needles, m. p. 210°. The 2 : 3-*dinitro*-p-*anisidide* also forms a substitution *compound* with aniline, $C_{20}H_{18}O_7N_4S$, red needles, m. p. 175—176°. E. H. R.

Sulphur Phenyl Chloride [Chlorothiolbenzene]. H. LECHER and F. HOLSCHNEIDER (*Ber.*, 1924, **57**, [*B*], 755—758; cf. Zincke and Baeumer, A., 1918, i, 537).—The simplest member of the series of sulphur aryl chlorides discovered by Zincke (cf. A., 1912, i, 763) has been obtained by converting phenylthiol thiocyanate (A., 1922, i, 641) with diethylamine in ethereal solution into *diethylaminothiolbenzene* (*benzenesulphendiethylamide*), $SPh{\cdot}NEt_2$, colourless fluid, b. p. 90°/3·5 mm., which on treatment with hydrogen chloride in absolute ether yields *chlorothiolbenzene*, PhSCl, a red, fuming liquid, b. p. 73—75°/9 mm. Chlorothiolbenzene can also be obtained by the action of chlorine on thiophenol or diphenyl disulphide in carbon tetrachloride solution. Chlorothiolbenzene closely resembles sulphur dichloride both in odour and in absorption spectrum. Its constitution follows from its reaction with diethylamine to give diethylaminothiolbenzene, with zinc dust giving diphenyl disulphide, and with β-thionaphthol yielding phenyl β-naphthyl disulphide. R. B.

Interconversion of some Isomeric Cyclic *cis*- and *trans*-1 : 2-Glycols. P. H. HERMANS (*Ber.*, 1924, **57**, [*B*], 824—827).—During the investigation of the equilibrium proportions of the *cis*- and *trans*-isomerides of certain glycols, viz., hydrindene-1 : 2-diol, tetrahydronaphthalene-1 : 2-diol and -2 : 3-diol, by the acetone method (cf. A., 1921, i, 663), it was found that equilibrium constants could not be obtained, the *cis*-diol obtained by hydrolysing the acetone compound with boiling dilute acid being partly converted into, and therefore contaminated with, the *trans*-isomeride. The reverse transformation occurs on boiling the pure *trans*-diol with dilute acid, and in boiling dilute acid solution the three 1 : 2-glycols named give equilibrium mixtures of the *cis*- and *trans*-forms. The pure *cis*-isomerides are obtained when the hydrolysis of the acetone compound is carried out with 1·5% sulphuric acid in aqueous acetone below 50°. From the fact that isomerisation does not occur during the formation or hydrolysis of the acetone compound, it is deduced that in these reactions only the O—H linkings of the glycol are concerned and not the C—O linkings, an observation which has some significance for the mechanism of the mutarotation of sugars. The isomerisation was not observed in the case of *cyclo*hexane-1 : 2-diol. R. B.

Derivatives of *iso*-α-Naphthyl-1 : 4-dihydroxy-β-naphthyl-sulphone. II. O. HINSBERG (*Ber.*, 1924, **57**, [*B*], 838—840; cf. A., 1919, i, 202).—By crystallising α-naphthyl-1 : 4-dihydroxy-β-naphthylsulphone twice from acetic acid the yield of *iso*-α-naphthyl-2-α-naphthaquinonylsulphoxide is considerably improved and the by-product melting at 225° is not formed. The sulphoxide is also formed when the dihydroxysulphone is boiled in acetic acid solution for 6 hours. By reduction with zinc dust and sodium hydroxide in the presence of ammonia, the sulphoxide yields a grey substance, changing to bright yellow crystals, m. p. 110°. Reduction of the *iso*-α-naphthyl-2-α-naphthaquinonylsulphone (obtained by oxidation of the sulphoxide, A., 1919, i, 202), with

sulphurous acid and hydriodic acid in acetic acid solution, regenerates the *iso*sulphoxide. The sulphoxide and sulphone are distinguished by their behaviour with ammoniacal methyl alcohol. The sulphone dissolves readily and the solution remains clear on dilution, whilst the sulphoxide only partly dissolves on boiling, and the bright yellow solution becomes turbid on adding water. Sodium hydroxide converts the sulphone into a *substance*, $C_{20}H_{11}O_5SNa_2,0{\cdot}5H_2O$, bright yellow needles, probably the sodium salt of *iso*-α-naphthyl-2-α-hydroxynaphthaquinonylsulphone, $C_{10}H_7{\cdot}SO_2{\cdot}C_{10}H_4O_2(OH)$. Compounds of the *iso*-series crystallise from chloroform with 0·5 mol. of solvent. R. B.

Configuration of the Hydrobenzoins in Connexion with the Situation of the Hydroxyl Groups in Space. J. Böeseken and P. H. Hermans (*Proc. K. Akad. Wetensch.*, 1924, **27**, 178—183).—Substitution of hydrogen atoms attached to the α-carbon atom of α-hydroxy acids by alkyl or phenyl groups renders the two hydroxyl groups more readily accessible to boric acid. That this substitution also favours the formation of cyclic acetone compounds is indicated by Willstätter and Königsberger's observations (A., 1923, i, 1172).

The effects of inactive and racemic hydrobenzoins on the conductivity of boric acid are analogous to those produced by esters of tartaric acid, from which it is concluded that the mutual repulsion of the phenyl groups exceeds that of the hydroxyl groups, and the hydroxyl groups in racemic hydrobenzoin are consequently strongly inclined towards each other. These results are discussed in their relationship to those previously obtained. T. H. P.

Semipinacolinic Transformation of Arylhydrobenzoins. Comparative Migratory Tendencies of Naphthyl and Phenyl Radicals. A. Orékhoff and M. Tiffeneau (*Compt. rend.*, 1924, **178**, 1619—1621).—In the pinacolinic transposition, the naphthyl radical, like all substituted phenyl radicals, tends to migrate more readily than the phenyl group itself. To ascertain if this is the case also in the semipinacolinic conversion, the authors have investigated the two reactions: (I) $C_{10}H_7{\cdot}CPh(OH){\cdot}CHRI \xrightarrow[-HI]{+AgNO_3} C_{10}H_7{\cdot}CPh(O{\cdot}){\cdot}CHR{\cdot}$, and (II) $C_{10}H_7{\cdot}CPh(OH){\cdot}CHR{\cdot}OH \xrightarrow[-H_2O]{H_2SO_4} C_{10}H_7{\cdot}CPh(O{\cdot}){\cdot}CHR{\cdot}$.

Reaction (I) yielded no useful result since, in each of the instances examined, the action of silver nitrate causes loss, not of HI, but of HOI, the hydrocarbon used for preparing the iodohydrin being regenerated. As regards reaction (II), concentrated sulphuric acid converts αβ-dihydroxy-αβ-diphenyl-β(α-naphthyl)ethane into α-naphthyldeoxybenzoin, m. p. 108—109°. This ketone was obtained by McKenzie and Roger (T., 1924, **125**, 845), who did not, however, fix its constitution; the latter is evident from the fact that it yields benzoic acid and phenyl-α-naphthylmethane when treated with alcoholic potassium hydroxide. Evidently the

action of the sulphuric acid results in elimination of the secondary hydroxyl group and in semipinacolinic transposition:

$C_{10}H_7 \cdot CPh(OH) \cdot CHPh(OH) - H_2O \longrightarrow COPh \cdot CHPh \cdot C_{10}H_7$.

That the reaction takes place in this manner is rendered more probable by the fact that McKenzie and Richardson (T., 1923, 123, 79) obtained the same ketone by the action of nitrous acid on the amino-alcohol corresponding with αβ-dihydroxy-αβ-diphenyl-β(α-naphthyl)ethane, by so-called "semipinacolinic de-amination."

T. H. P.

Insecticides. VII. Syntheses of Chrysanthemumic Acid and other *cyclo*Propanecarboxylic Acids with Unsaturated Side Chains. H. STAUDINGER, O. MUNTWYLER, L. RUZICKA, and S. SEIBT (*Helv. Chim. Acta*, 1924, **7**, 390—406).—The monocarboxylic acid obtained from pyrethrine I, one of the active constituents of insect powder (this vol., i, 510), and identified as 2 : 2-dimethyl-3-*iso*butenyl*cyclo*propane-1-carboxylic acid, has been synthesised by condensing βε-dimethyl-$\Delta^{\beta\delta}$-hexadiene with ethyl diazoacetate. (The hexadiene was obtained in a novel manner by distilling βε-dichloro-βε-dimethylhexane with soda-lime.) A mixture of *cis*- and *trans*-acids was thus obtained, forming a colourless oil, b. p. 140—145°/12 mm., from which on cooling the *cis*-isomeride gradually separated, m. p. 115—116°. The *trans*-isomeride was only obtained in an impure form, b. p. 145—146°/13 mm. By the action of ozone, the two isomerides give, respectively, *cis*- and *trans*-caronic acid. Both acids give insecticidal esters with pyrethrolone, that from the *trans*-acid being the more active. The natural ester is from the d-*trans*-acid, but the synthetic acid has not yet been resolved. A number of related acids were also synthesised, using other butadiene derivatives, but only those from βγ-dimethylbutadiene and isoprene gave insecticidal esters with pyrethrolone, and these were weaker than the true pyrethrines. Purely aliphatic acids of similar structure but without the *cyclo*propane ring, such as βζ-dimethyl-Δ^{ϵ}-heptene-γ-carboxylic acid, $CHMe_2 \cdot CH(CO_2H) \cdot CH_2 \cdot CH{:}CMe_2$, do not form insecticidal esters.

By the action of ethyl diazoacetate on βδ-dimethyl-$\Delta^{\beta\delta}$-hexadiene an ester was obtained which on hydrolysis gave an *acid*, $C_{10}H_{16}O_2$, b. p. 140—145°/13 mm., which appeared to be a mixture of isomerides. Using β-methyl-$\Delta^{\beta\delta}$-hexadiene and βδ-dimethyl-$\Delta^{\alpha\gamma}$-pentadiene, mixed products were also obtained. From ethyl diazoacetate and βγ-dimethylbutadiene, *2-methyl-2-isopropenylcyclopropanecarboxylic acid*, b. p. 122—123°/15 mm., was obtained; *chloride*, b. p. 90°/11 mm. By oxidation with ozone followed by permanganate, the acid gave a *methylcyclopropanedicarboxylic acid*, m. p. 168—169°. Ethyl diazoacetate and $\Delta^{\beta\delta}$-hexadiene give *2-methyl-3-propenylcyclopropanecarboxylic acid*, a liquid, b. p. 126°/9 mm.; *chloride*, b. p. 86°/9 mm. Isoprene and ethyl diazoacetate give trans-2-iso*propenylcyclopropanecarboxylic acid*, a colourless oil, b. p. 115—119°/12 mm.; *chloride*, b. p. 62—64°/13 mm. From its ozonide was obtained *2-acetylcyclopropanecarboxylic acid*, crystals, m. p. 52—54° (*semicarbazone*, m. p. 177—179°). Further oxidation

with permanganate gives *trans-cyclo*propane-1 : 2-dicarboxylic acid. Hydrocarbons of the terpene series also condense with ethyl diazoacetate to give *cyclo*propanecarboxylic acid derivatives of uncertain constitution.

By condensing ethyl methylmalonate with dimethylallyl bromide, *αδ-dimethyl-Δ$^{\nu}$-hexenoic acid* was obtained, b. p. 125°/15 mm.; *chloride*, b. p. 80—85°/12 mm. *βζ-Dimethyl-Δ$^{\epsilon}$-heptene-γ-carboxylic acid*, from dimethylallyl bromide and ethyl *iso*propylmalonate, is a colourless oil, b. p. 140—145°/12 mm.; *chloride*, b. p. 115°/10 mm. *β-Methyl-Δ$^{\beta\eta}$-octadiene-ε-carboxylic acid*,

$$CMe_2{:}CH{\cdot}CH_2{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CH{:}CH_2,$$

colourless oil, b. p. 137—138°/10 mm., is obtained from dimethylallyl bromide and ethyl allylmalonate; *chloride*, b. p. 84°/10 mm.

E. H. R.

Modification of the Sandmeyer Synthesis of Nitriles. H. T. Clarke and R. R. Read (*J. Amer. Chem. Soc.*, 1924, **46**, 1001—1003).—A method of preparing nitriles which avoids the evolution of hydrogen cyanide is described. The diazonium solution is neutralised by means of sodium carbonate at 0—4° and poured into a similarly cooled solution of sodium cuprocyanide, the surface of which is first covered with a layer of benzene. With good stirring, the benzene (in which the nitrile is soluble) is drawn beneath the surface and a rise in temperature prevented. Yields of nitriles up to 60—70% of the theoretical were obtained using aniline, *o*-toluidine, *p*-toluidine, and other amines. In the absence of the benzene, the reaction product comes to the surface as a dark brown oil, in which, after a few moments, a vigorous action is set up and fumes smelling of phenylcarbylamine are given off. A. C.

Electrochemical Reductions in Acid Solution. K. Kindler, O. Giese, and A. Isberg (*Ber.*, 1924, **57**, [*B*], 773—775).—An examination of the reduction of phenylacetamide, phenylthioacetamide, and their *N*-alkyl derivatives shows that the more *N*-methyl groups there are present the more rapid is the electrochemical reduction and the slower the reduction by aluminium amalgam. The figures in brackets give the percentage of the theoretical yield of amine formed by reduction of the corresponding amide. (I) Electrochemical reduction (cf. A., 1923, i, 568, 1090): $CH_2Ph{\cdot}CO{\cdot}NH_2$ (<1%); $CH_2Ph{\cdot}CO{\cdot}NHMe$ (80%); $CH_2Ph{\cdot}CO{\cdot}NMe_2$ (92%); $CH_2Ph{\cdot}CS{\cdot}NHMe$ (80%); $CH_2Ph{\cdot}CS{\cdot}NMe_2$ (100%). No phenylacetaldehyde was observed as a by-product. (II) Reduction with aluminium amalgam : $CH_2Ph{\cdot}CS{\cdot}NH_2$ (74%); $CH_2Ph{\cdot}CS{\cdot}NHMe$ (2%); $CH_2Ph{\cdot}CS{\cdot}NMe_2$ (<1%). During the electrolysis of an aqueous-alcoholic hydrochloric acid solution of phenylacetdimethylamide, its concentration around the cathode increased, whereas with phenylacetamide no such increase was noted. It is suggested that during electrolysis of the strongly acid solution the first stage is the addition of acid to form the ammonium or oxonium salts, the cations of which, after giving up their charge, are converted into free radicals which then readily undergo reduction at the cathode. F. A. M.

Syntheses by means of Sodamide. Preparation of Benzyl Phenylalkylacetates and the Corresponding Acids. (MME.) RAMART and A. HALLER (*Compt. rend.*, 1924, **178**, 1583—1587; cf. this vol., i, 171, 286).—At the ordinary temperature, the action of sodamide on phenyl formate yields sodium phenoxide, ammonia, and carbon monoxide, and on phenyl acetate, sodium phenoxide and acetamide. Treatment of benzyl *iso*butyrate in xylene solution with sodamide and then with benzyl chloride yields *N*-benzyl-*iso*butyramide and another compound, m. p. 65—66°, of unknown constitution.

With benzyl phenylacetate, a similar reaction occurs, the temperature gradually rising and phenylacetamide and phenylacetbenzylamide being formed. If, however, the reaction is carried out at 0° and the flask is connected through a reflux condenser with a vacuum pump so as to facilitate the disengagement of ammonia, little amide is formed but instead the sodium derivative of the ester, $C_7H_7{\cdot}O{\cdot}CO{\cdot}CHPhNa$ or $C_7H_7{\cdot}O{\cdot}C(ONa){:}CHPh$; when the evolution of ammonia becomes very slight, the alkyl or benzyl halide is added gradually, the product being finally treated with water and the mixture of esters rectified in a vacuum.

Benzyl α-phenylpropionate (hydratropate), formed under these conditions, could not be separated from the benzyl phenylacetate, but is readily separated as acid (cf. Fittig and Wurster, A., 1879, 379). *Benzyl phenylallylacetate*, similarly obtained, forms an oil, b. p. 210—212°/25 mm. (cf. Buddeberg, A., 1890, 1142). *Benzyl benzylphenylacetate* is a yellow, oily liquid, b. p. 250—255°/18 mm.

T. H. P.

Higher Terpene Compounds. XXII. *l*-Pimaric Acid. L. RUZICKA, F. BALAS, and F. VILIM (*Helv. Chim. Acta*, 1924, **7**, 458—471).—Improved methods for obtaining *l*-pimaric acid from galipot are described, consisting in fractionally crystallising the resinic acids from acetone, a procedure which may be preceded by fractional crystallisation of the sodium salts (cf. Dupont, A., 1921, i, 510). *l*-Pimaric acid is more stable in the form of its sodium salt than *d*-pimaric acid. Hydrogenation experiments show that *l*-pimaric, like abietic acid, has two double bonds (cf. A., 1923, i, 818). *Dihydro-l-pimaric acid* is obtained by hydrogenation of *l*-pimaric acid with colloidal platinum and hydrogen in ethyl acetate; it consists apparently of a mixture of isomerides, the first fraction of which, from alcohol, forms crystals, m. p. 142—144°, $[\alpha]_D$ +24° in 1% alcoholic solution. More energetic hydrogenation by the method of Willstätter and Waldschmidt-Leitz (A., 1921, ii, 185) resulted in the formation of *tetrahydro-l-pimaric acid*, a mixture of isomerides, m. p. 120—160°. The molecular refractions of the esters of *l*-pimaric acid also indicate the presence of two double bonds; the *methyl* ester is a viscous oil, b. p. 166—169°/0·5 mm., $[\alpha]_D$ −190·36° in 5% alcoholic solution, d_4^{22} 1·0312; n_D^{22} 1·5232; when kept, the oil formed long crystals, m. p. 57°; the *ethyl* ester is a viscous oil, b. p. 175—177°/0·5 mm., $[\alpha]_D$ −170·9° in 6% alcoholic solution, d_4^{23} 1·0124; n_D^{23} 1·5153.

When *l*-pimaric acid is heated in boiling acetic acid, an isomeride is formed, m. p. 167—168°, $[\alpha]_D$ −103·7°, corresponding in crystalline form with abietic acids from various sources, whilst by heating at 300° it is converted into an isomeride, m. p. 175—176°, $[\alpha]_D$ +22·3°, corresponding with abietic acid from American colophony, m. p. 178—179°, $[\alpha]_D$ +3° (A., 1922, i, 547). It is concluded, therefore, that *l*-pimaric acid belongs to the group of spatially isomeric abietic acids. *d*-Pimaric acid is a structural isomeride and does not belong to the abietic acid group. In agreement with this view, *l*-pimaric acid gives retene when dehydrogenated with sulphur, and resembles abietic acid in other respects. E. H. R.

***iso*Fenchocarboxylic Acid.** S. Nametkin and A. Ruschentzev (*J. pr. Chem.*, 1923, **106**, 39—40).—The acid is prepared by passing dry carbon dioxide into a cold solution of *iso*fenchone in ether in the presence of sodium wire. After the vigorous reaction has subsided, the mixture is heated for 3 days. The ether is then evaporated, excess of sodium removed, and the residue decomposed by water. The viscid residual mass is washed with ether, acidified with sulphuric acid, and the acid purified through its sodium salt. It melts at 87—88° with evolution of carbon dioxide. With ferric chloride, it yields a dark blue coloration, rapidly turning dirty green. The acid decomposes rapidly, even in the dark, yielding *iso*fenchone and a white solid, m. p. 230—231°. F. G. P.

Action of Sodium Hydrogen Sulphite on Chlorides of the Hydroximic Acids. VII. C. Gastaldi (*Gazzetta*, 1924, **54**, 220—226).—The ready replacement of the chlorine atom by hydroxyl observed when chloroximinoacetone is treated with sodium hydrogen sulphite (cf. A., 1923, i, 1236) occurs also in other similar cases and furnishes a means of preparing hydroxamic acids not obtainable by the ordinary methods.

Benzoylformhydroxamic acid, COPh·CO·NH·OH or OH·CBz:NOH, prepared from α-chloro-α-oximinoacetophenone, forms stable, colourless prisms or pink laminæ, m. p. 117° (decomp.), and forms two *oximes*: (1) the *α-modification*, NOH:CPh·CO·NH·OH or NOH:CPh·C(OH):NOH, crystallises in colourless prisms, m. p. 177° (decomp.), and in aqueous solution gives with nickel acetate and ammonia a green precipitate soluble in dilute acetic acid; (2) the *β-modification*, prepared by the action of sodium hydrogen sulphite on benzoylformhydroximic chloride oxime (chlorophenylglyoxime) (cf. Ponzio and Avogadro, A., 1923, i, 472), forms pale yellow laminæ, m. p. 189° (decomp.), and differs from the α-form in giving with nickel acetate a brick-red precipitate insoluble in dilute acetic acid or ammonia solution. *Benzoylformhydroxamic acid phenylhydrazone*, $C_{14}H_{13}O_2N_3$, crystallises in yellow needles, m. p. 127°. T. H. P.

3 : 4 : 5-Trihydroxycinnamic Acid and the Mechanism of Knoevenagel's Cinnamic Acid Synthesis. K. W. Rosenmund and T. Boehm (*Annalen*, 1924, **437**, 125—147).—Gallaldehyde on warming with one or two mols. of aniline and malonic acid in

alcoholic solution yields a yellow solid which on heating at 155—160° melts with evolution of carbon dioxide. Treatment with hydrochloric acid converts the substance into the known hydrochloride of gallaldehyde-aniline, an additive compound, not a Schiff's base. The yellow solid proves to be a normal malonate of the aldehyde-aniline, $[C_6H_2(OH)_3\cdot CH(OH)\cdot NHPh]_2,CH_2(CO_2H)_2$, and the expected trihydroxycinnamic acid could not be obtained from this reaction. Protocatechualdehyde behaves similarly, and these results suggest that the primary product in the reaction is not a benzylidenemalonic acid, as Knoevenagel suggested (A., 1899, i, 144), but a benzylideneaniline (cf. Dimroth and Zoeppritz, A., 1902, i, 292). These additive products form stable salts with strong acids (cf. Dimroth, A., 1902, i, 292), and do not react with malonic acid to give substituted acrylic acids. The Schiff's bases do not form stable salts, but react with malonic acid, yielding substituted acrylic acids. The formation of acrylic acid derivatives is thus conditional on the existence of a double bond between carbon and nitrogen, and it is suggested that the malonic acid attacks the molecule at this point: $CHPh{:}NPh+CH_2(CO_2H)_2\rightarrow NHPh\cdot CHPh\cdot CH(CO_2H)_2$. The resulting β-anilinodicarboxylic acid is unstable (cf. Goldstein, A., 1895, i, 470; 1896, i, 435) and easily loses carbon dioxide, yielding a β-substituted β-anilinopropionic acid, *e.g.*, $NHPh\cdot CHPh\cdot CH_2\cdot CO_2H$, which is decomposed by mineral acid, yielding aniline and the corresponding acrylic acid. On this theory, the failure of attempts to prepare trihydroxycinnamic acid from gallaldehyde, aniline, and malonic acid is attributed to the weakly basic character of aniline as opposed to the relatively acidic gallaldehyde. When instead of aniline, the stronger base piperidine was used, 3 : 4 : 5-trihydroxycinnamic acid was obtained in good yield.

Attempts were also made to prepare trihydroxycinnamic acid by condensing gallaldehyde with malonic acid derivatives. Ethyl malonate and cyanoacetic acid gave no result, but with malononitrile gallaldehyde yields ββ-*dicyano*-3 : 4 : 5-*trihydroxystyrene*, $C_6H_2(OH)_3\cdot CH{:}C(CN)_2$, m. p. 250° (decomp.), which by acid hydrolysis is converted into α-cyano-3 : 4 : 5-trihydroxycinnamamide, $C_6H_2(OH)_3\cdot CH{:}C(CN)\cdot CO\cdot NH_2$. On further hydrolysis, this yields α-cyano-3 : 4 : 5-trihydroxycinnamic acid, but the hydrolysis of the second cyano group could not be effected. Condensation of gallaldehyde with rhodanine gave a trihydroxybenzylidenerhodanine, $C_6H_2(OH)_3\cdot CH{:}C<\begin{matrix}S-CS\\CO\text{-}NH\end{matrix}$, but attempts to prepare from this α-thioltrihydroxycinnamic acid were unsuccessful.

ββ-*Dicyano*-3 : 4 : 5-*triacetoxystyrene* (from triacetylgallaldehyde and malononitrile) has m. p. 139—140°. ββ-*Dicyano*-3 : 4-*dihydroxystyrene* forms yellow needles, m. p. 221° (decomp.); *acetyl* derivative, m. p. 110—111°. Hydrolysis with 38% hydrochloric acid converts the dicyanotrihydroxystyrene into α-cyano-3 : 4 : 5-trihydroxycinnamamide, reddish-yellow needles, m. p. 268° (decomp.), which was also obtained by condensation of gallaldehyde with cyanoacetamide; *triacetyl* derivative, m. p. 210—211°. α-*Cyano*-3 : 4-*di*-

acetoxycinnamamide has m. p. 196—198°. Condensation of gallaldehyde with ethyl cyanoacetate in the presence of sodium ethoxide yields *ethyl α-cyano-3 : 4 : 5-trihydroxycinnamate*, yellow needles, m. p. 201—202° (*triacetyl* derivative, m. p. 142°), which on careful hydrolysis with dilute sodium hydroxide yields *α-cyano-3 : 4 : 5-trihydroxycinnamic acid*, small, pale yellow plates, m. p. 210—212° (decomp.); *triacetyl* derivative, m. p. 180°. Protocatechualdehyde similarly yields *ethyl α-cyano-3 : 4-dihydroxycinnamate*, yellow needles, m. p. 168° (*diacetyl* derivative, m. p. 97°), which by alkaline hydrolysis gives *α-cyano-3 : 4-dihydroxycinnamic acid* (*α-cyano-caffeic acid*), yellow plates, m. p. 224—225° (decomp.); *diacetyl* derivative, m. p. 195—196°.

Gallaldehyde condensed with rhodanine in the presence of sodium hydroxide yields amorphous 3 : 4 : 5-*trihydroxybenzylidenerhodanine*, which gives a crystalline *triacetyl* compound, m. p. 222—223°. Similarly, protocatechualdehyde and rhodanine (in alcoholic sulphuric acid) yield 3 : 4-dihydroxybenzylidenerhodanine, small, yellowish-brown tablets, m. p. 270—280° (decomp.); *diacetyl* derivative, m. p. 217—218°. Phenylrhodanine gives *phenyl-3 : 4-dihydroxybenzylidenerhodanine*, $C_6H_3(OH)_2\cdot CH{:}C\begin{matrix}S{-}CS\\ \\ CO{-}NPh'\end{matrix}$ dense yellow lances, m. p. 268—270° (decomp.); *diacetyl* derivative, m. p. 195°. Gallaldehyde and aniline in alcoholic solution give with hydrogen chloride a yellow precipitate of *gallaldehydeaniline* (*hydroxy-3 : 4 : 5-trihydroxyphenylmethylaniline*) *hydrochloride*, $C_6H_2(OH)_3\cdot CH(OH)\cdot NHPh,HCl$, m. p. 226°, which does not lose water at 130°. The free *base* crystallises in yellow needles ($+1H_2O$), which lose water at 80° and melt at 190—192°, yielding the Schiff's base, 3 : 4 : 5-*trihydroxybenzylideneaniline*, which on warming with hydrochloric acid is reconverted into the gallaldehydeaniline hydrochloride. The *malonate* (*supra*) forms yellow needles, m. p. 171°. *Protocatechualdehydeaniline hydrochloride* forms fine, yellowish-brown needles, m. p. 231—232°; *malonate*, m. p. 173°.

3 : 4 : 5-*Trihydroxycinnamic acid* forms colourless needles ($+1H_2O$), m. p. 207—208°; the water is lost at 120°; *triacetyl* derivative, needles, m. p. 168°. The acid is distinguished from gallic acid and gallaldehyde by its ferric chloride reaction (dark green coloration, changing to clear yellow on dilution) and by the fine carmine-red to violet coloration produced with potassium cyanide. With bromine (2 mols.) in acetic acid solution, the trihydroxycinnamic acid yields a *dibromo* derivative, $C_9H_6O_5Br_2$, colourless needles, m. p. 186—187°, probably 2 : 6-dibromo-3 : 4 : 5-trihydroxycinnamic acid. The triacetyl derivative similarly yields the corresponding *dibromotriacetoxycinnamic acid*, $C_{15}H_{12}O_8Br_2$, long tablets, m. p. 183°. R. B.

Preparation of *p-iso*Propylphenylacetaldehyde and some of its Isomerides and Homologues. P. CHUIT and J. BOLLE (*Bull. Soc. chim.*, 1924, [iv], **35**, 200—205).—*p-iso*Propylphenylacetaldehyde (cf. A., 1923, i, 1101) may be prepared as a colourless liquid, b. p. 116·5—117°/11 mm., d^{15} 0·980, n_D^{20} 1·51071, by con-

densing cumaldehyde with ethyl chloroacetate in presence of sodium ethoxide. The product is hydrolysed and then steam-distilled in presence of excess of oxalic acid solution. The semicarbazone melts at 172°, not at 181° (cf. Bert, *loc. cit.*). The aldehyde polymerises to a viscous oil on standing. In a similar manner, from 2 : 4 : 6-trimethylbenzaldehyde, 2 : 4 : 6-*trimethylphenylacetaldehyde* is obtained, m. p. 61°, b. p. 137—140°/13 mm., having a faint disagreeable odour. 3 : 4 : 6-*Trimethylphenylacetaldehyde* is a colourless liquid, b. p. 127—129°/15 mm., d^{15} 0·998, n_D^{15} 1·5311; *semicarbazone*, m. p. 191°.

By the condensation of ethyl chloroglyoxylate with *p*-cymene in presence of aluminium chloride, ethyl cymylglyoxylate is formed (b. p. 175—180°/12 mm.) which, on conversion into the acid and boiling with excess of aniline, forms the phenylimide (b. p. 200—202°/14 mm.). By warming the latter with dilute hydrochloric acid, 6-*methyl*-3-iso*propylbenzaldehyde* is obtained, a colourless liquid, b. p. 121—121·3°/14 mm., d^{15} 0·978, n_D^{15} 1·5108. Condensation of this with chloroacetic acid as above yields 2-p-*cymylacetaldehyde*, b. p. 128·5—129°/13 mm., d^{15} 0·967, n_D^{15} 1·5175; *semicarbazone*, m. p. 160°.

Poor yields of m-*cymylaldehyde* (2-*methyl*-4-iso*propylbenzaldehyde*) are obtained from *m*-cymene by Gattermann's synthesis. It is a liquid, b. p. 115—118°/13 mm., d^{15} 0·972; *semicarbazone*, m. p. 198—199°. It oxidises in air to a steam-volatile cymylcarboxylic acid, m. p. 77·5°, which is also one product of oxidation by boiling dilute nitric acid. The other product is 3-methylterephthalic acid, the formation of which proves the constitution of the original compound. 2-m-*Cymylacetaldehyde*, prepared by the above general method, is a colourless liquid, b. p. 123—126°/12 mm., d^{15} 0·973, n_D^{15} 1·5203, *semicarbazone*, m. p. 158—159°. E. E. T.

Isomerisation of Nitroaldehydes by Chemical Means. G. Heller (*J. pr. Chem.*, 1923, **106**, 1—16).—*o*-Nitrobenzaldehyde on exposure to light in indifferent solvents is converted into *o*-nitrosobenzoic acid, in alcoholic solution into the related esters. Similarly, on exposure to light in absolute hydrocyanic acid, the nitrosobenzoic acid results, whilst *o*-nitromandelonitrile under the same conditions loses hydrogen cyanide and gives the acid. The question whether oxygen can be thus transferred from the nitro to the aldehyde group by chemical methods has not been satisfactorily settled. It has been found that potassium cyanide reacts with an aqueous-alcoholic solution of *o*-nitrobenzaldehyde readily in the cold, necessitating external cooling, *o*-nitrosobenzoic acid being found in the reaction product, and ammonium *o*-nitrosobenzoate is obtained by dissolving *o*-nitromandelonitrile in alcoholic ammonia. The conversion of *o*-nitrobenzaldehyde into the nitrosobenzoic acid without isolating the nitromandelonitrile is best accomplished by the action of a solution of potassium cyanide and ammonium acetate in concentrated ammonia on an alcoholic solution of the nitrobenzaldehyde, almost pure ammonium nitrosobenzoate being precipitated. *o*-Nitromandelonitrile is probably

first produced by the action of potassium cyanide, and loses hydrogen cyanide, forming *o*-nitrosobenzoic acid at the same time. Ekecrantz and Ahlqvist (A., 1908, i, 347) by the action of potassium cyanide on a hot alcoholic solution of the *o*-nitroaldehyde obtained azoxybenzoic acid and nitrosobenzoic acid, but since alkali does not act so smoothly on *o*-nitromandelonitrile as ammonia does, their investigation could not lead to a homogeneous result. By altering the conditions, it is found that small quantities of azoxybenzoic acid may be obtained. *o*-Nitropiperonal can be converted into the mandelonitrile by the action of potassium cyanide on its hydrogen sulphite compound, the nitrile produced yielding the nitroso-acid on treatment with alcoholic ammonia, or by the direct action of the alcoholic ammoniacal ammonium cyanide solution on the nitroaldehyde. The ammonium cyanide acts as an oxygen carrier since less than 1 mol. is sufficient. 2-Nitro-5-chlorobenzaldehyde and the corresponding 5-bromoaldehyde are readily converted into the nitroso-acids. Nitrohydroxyaldehydes give only resinous products, as do *o*-nitrovanillin and nitroterephthalaldehyde. In all these cases also, no cyanohydrin could be obtained from the aldehyde. 2 : 4-Dinitrobenzaldehyde reacts normally with ammonium cyanide to give 4-nitro-2-nitrosobenzoic acid, but by the action of potassium cyanide in glacial acetic acid solution yields 2-nitro-4-nitrosobenzoic acid. No analogous compounds were obtained from trinitrobenzaldehyde. Attempts to carry out the reaction with such substances as β-*o*-nitrophenyllactonitrile, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot CH(OH)CN$, and γ-*o*-nitrocinnamylglycollonitrile, $NO_2 \cdot C_6H_4 \cdot CH{:}CH \cdot CH(OH)CN$, gave negative results either with the nitriles themselves or with the parent nitroaldehydes. Oxygen is therefore not capable of migrating into the side chain from a neighbouring nitro group. *o*-Nitrophenyl-lactonitrile has been converted into the acid amide by hydrolysis with 75% sulphuric acid, and the amide into the acid by heating with concentrated sulphuric acid and glacial acetic acid. By reduction of the acid with zinc dust and hydrochloric acid, 3-hydroxycarbostyril is produced.

m-Nitroaldehydes behave quite differently, yielding only amorphous products. 2-Chloro-5-nitrobenzaldehyde in glacial acetic acid solution yields a cyanohydrin, but from this only a compound of complex type was obtained by the use of the alcoholic ammoniacal ammonium cyanide solution. With *p*-nitrobenzaldehyde, an amorphous product was obtained.

A repetition of the work of Ekecrantz and Ahlqvist (*loc. cit.*) showed that *o*-nitrobenzaldehyde in the presence of a small quantity of potassium cyanide does not yield azoxybenzoic acid, but that *o*-nitrosobenzoic acid and a compound, $C_{14}H_8O_6N_2$ (in very small yield), m. p. 162—163°, are produced. On the other hand, by increasing the amount of potassium cyanide, *o*-nitrosobenzoic acid, the compound $C_{14}H_8O_6N_2$, and azoxybenzoic acid are obtained.

[With H. KRETZSCHMANN.]—o-*Nitropiperonalcyanohydrin*, $C_9H_6O_5N_2$, crystallises in pale yellow needles, m. p. 119°. o-*Nitrosopiperonylic acid*, $C_8H_5O_5N$, a yellow, crystalline powder, sinters at 160—165°, and melts at about 198°.

[With H. GRUNDMANN.]—5-*Bromo*-2-*nitrosobenzoic acid* crystallises in pale brown needles, m. p. 173°. 4-*Nitro*-2-*nitrosobenzoic acid*, $C_7H_4O_5N_2$, from 2 : 4-dinitrobenzaldehyde, has m. p. above 300°; its *methyl* ester crystallises in silky needles, m. p. 137° to a green liquid. 2-*Nitro*-4-*nitrosobenzoic acid* is a yellow, crystalline solid, m. p. about 230°. On oxidation with fuming nitric acid, it yields dinitrobenzoic acid. Its *methyl* ester crystallises in yellow needles, m. p. 141° to a green liquid. β-o-*Nitrophenyl-lactonitrile*, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot CH(OH)CN$, from the hydrogen sulphite compound of *o*-nitrophenylacetaldehyde, crystallises in plates, m. p. 70—71°. On hydrolysis with 75% sulphuric acid, it is converted into the *lactamide*, $C_9H_{10}O_4N_2$, needle aggregates, m. p. 195°. By heating the lactamide in glacial acetic acid with excess of concentrated sulphuric acid, o-*nitrophenyl-lactic acid* is obtained, nearly colourless needles, m. p. 72°.

[With H. JÜRGENS.]—o-*Nitrocinnamylglycollonitrile*, $C_{10}H_8O_3N_2$, obtained by the action of absolute hydrocyanic acid on *o*-nitrocinnamaldehyde, has m. p. 79°. By the action of alcoholic ammonia, hydrocyanic acid is eliminated and tarry products are obtained. Dilute solutions of sodium hydroxide regenerate the aldehyde.

[With K. MÜLLER-BARDOFF.]—2-*Chloro*-5-*nitromandelonitrile*, obtained by the action of potassium cyanide on a glacial acetic acid solution of the corresponding aldehyde, crystallises in scales, m. p. 124°. Alcoholic ammonia converts it into a complex, crystalline substance, m. p. 303°, containing 15·4% N, insoluble in acids and alkalis and scarcely soluble in any of the organic solvents.

F. G. P.

Mercuration of Nitrohydroxybenzaldehydes. T. A. HENRY and T. M. SHARP (*J. Chem. Soc.*, 1924, **125**, 1049—1060; cf. A., 1923, i, 726).—The previously described *m*-hydroxyacetoxymercuribenzaldehyde (T., 1922, **121**, 1059) is now shown to be the 2-acetoxymercuri compound, from its conversion into 2-nitro-3-hydroxybenzaldehyde and into an iodo-*m*-hydroxybenzaldehyde yielding 2 : 3-dihydroxybenzoic acid on heating with sodium hydroxide.

The work has been extended to the nitrobenzaldehydes, which did not yield mercury derivatives, and to the nitrohydroxybenzaldehydes. The mercuration is effected by boiling with mercuric acetate and a small amount of acetic acid in 50% alcoholic solution. The dimercuri compounds obtained from 6-nitro-, 4-nitro-, and 2-nitro-3-hydroxybenzaldehyde on treatment with bromine all yield 2 : 4-dibromo-6-nitro-3-hydroxybenzaldehyde, the nitro groups in the 2 and 4 positions changing places with the bromine atom, which replaces mercury in position 6. The reaction with iodine is normal.

Mercuration of 3-nitro-4-hydroxybenzaldehyde yields only 3-*nitro*-4-*hydroxy*-5-*hydroxymercuribenzaldehyde*, small orange plates, darkening at 285°, but not melting at 300°, which by solution in sodium hydroxide and precipitation with hydrochloric acid is

converted into 3-*nitro*-4-*hydroxy*-5-*chloromercuribenzaldehyde*, colourless needles, m. p. 226° (decomp.), and on crystallisation from acetic acid yields 3-*nitro*-4-*hydroxy*-5-*acetoxymercuribenzaldehyde*, colourless prisms, darkening at 250°. With iodine in potassium iodide solution, the hydroxymercuri compound yields 5-*iodo*-3-*nitro*-4-*hydroxybenzaldehyde*, yellow plates, m. p. 171—172°. Similarly, 6-nitro-3-hydroxybenzaldehyde yields first an orange solid, apparently a mixture of the diacetoxydimercuri and dihydroxydimercuri compounds, whilst from the mother-liquors mixtures of mono- and di-mercurated products are obtained. The orange solid by crystallisation from propionic acid is converted into 6-*nitro*-3-*hydroxy*-2 : 4-*dipropoxydimercuribenzaldehyde*, orange-yellow needles, exploding at 235°. Its solution in sodium hydroxide on treatment with hydrochloric acid precipitates 6-*nitro*-3-*hydroxy*-2 : 4-*dichlorodimercuribenzaldehyde*, colourless needles. The pale yellow 6-*nitro*-3-*hydroxychloromercuribenzaldehyde* obtained from the more soluble fractions decomposes at 198°, and with iodine solution yields an *iodo*-6-*nitro*-3-*hydroxybenzaldehyde*, yellow prisms, m. p. 206° (decomp.), and a small quantity of 2 : 4-*di-iodo*-6-*nitro*-3-*hydroxybenzaldehyde*, yellow prisms or needles, m. p. 142° (decomp.); *semicarbazone*, m. p. 214° (decomp.); *oxime*, m. p. 207—208° (decomp.). The di-iodo compound is formed almost quantitatively by the action of iodine on the dimercuri compound, a small quantity of a mercuric iodide additive *compound*, $2C_7H_3O_4NI_2,HgI_2$, m. p. 184° (decomp.), being also sometimes formed, and this on decomposition with hydrogen sulphide yields mercuric sulphide and 2 : 4-di-iodo-6-nitro-3-hydroxybenzaldehyde. The dimercurated compound on treatment with bromine in alcoholic solution yields 2 : 4-*dibromo*-6-*nitro*-3-*hydroxybenzaldehyde*, colourless prisms, m. p. 152·5° (decomp.), which on oxidation with alkaline permanganate is converted into 2 : 4-*dibromo*-6-*nitro*-3-*hydroxybenzoic acid*, colourless needles, m. p. 230° (decomp.), identical with the acid obtained by oxidising 2 : 4-dibromo-6-nitro-*m*-cresol.

4-Nitro-3-hydroxybenzaldehyde on mercuration yields an orange-coloured 4-*nitro*-3-*hydroxy*-*hydroxymercuriacetoxymercuribenzaldehyde*, which on crystallisation from formic acid is converted into 4-*nitro*-3-*hydroxy*-2 : 6-*diformoxydimercuribenzaldehyde*, pale yellow needles, darkening at 120°, exploding at 257°. From its solution in potassium hydroxide, hydrochloric acid precipitates 4-*nitro*-3-*hydroxy*-2 : 6-*dichlorodimercuribenzaldehyde*, pale yellow needles ($+1H_2O$), darkening at 240° (the anhydrous substance decomposes at 282°) and carbon dioxide precipitates 2 : 3-*anhydro*-4-*nitro*-3-*hydroxy*-2 : 6-*dihydroxydimercuribenzaldehyde*. From the more soluble fractions of the mercuration product, by extraction with formic acid, 4-*nitro*-3-*hydroxyformoxymercuribenzaldehyde*, m. p. 233—235°, is obtained. The 4-*nitro*-3-*hydroxypropoxymercuribenzaldehyde*, pale orange needles, and the 4-*nitro*-3-*hydroxychloromercuribenzaldehyde*, yellow powder, decomposing at 187°, were also prepared. Treatment with iodine converts the monomercurated compound into an *iodo*-4-*nitro*-3-*hydroxybenzaldehyde*, yellow needles, m. p. 185°. The dimercurated compound, on

treatment with bromine, yields the 2 : 4-dibromo-6-nitro-3-hydroxybenzaldehyde previously obtained from the dimercuri-6-nitrohydroxybenzaldehyde. 2 : 6-*Dibromo-4-nitro-3-hydroxybenzoic acid*, m. p. 209°, was obtained, together with 4 : 6-dibromo-2-nitrophenol, by the oxidation of 2 : 6-dibromo-4-nitro-*m*-cresol with alkaline potassium ferricyanide. On treatment with iodine solution, the dimercurated substance yields a *di-iodo-4-nitro-3-hydroxybenzaldehyde*, yellow needles, m. p. 122°, which on oxidation gives a *di-iodo-4-nitro-3-hydroxybenzoic acid*, yellow prisms, m. p. 249° (decomp.). This acid is identical with that obtained by oxidising with alkaline potassium ferricyanide the di-iodo-4-nitro-*m*-cresol (which by analogy should be the 2 : 6-di-iodo derivative) prepared by treating 4-nitro-*m*-cresol with iodine and mercuric oxide.

The mercuration of 2-nitro-3-hydroxybenzaldehyde similarly yields at first mainly *2-nitro-3-hydroxyhydroxymercuriacetoxymercuribenzaldehyde*, yellow amorphous, and then *2-nitro-3-hydroxydiacetoxydimercuribenzaldehyde*, pale yellow needles, from which the *2-nitro-3-hydroxydichlorodimercuribenzaldehyde*, pale green, gelatinous substance, decomp. at 236°, is obtained. From the mother-liquors by fractional crystallisation from acetic acid, *2-nitro-3-hydroxyacetoxymercuribenzaldehyde*, microscopic needles, was obtained. *2-Nitro-3-hydroxychloromercuribenzaldehyde*, yellow powder, decomposes at 207°. On treatment with bromine, the dimercurated substance gives 2 : 4-dibromo-6-nitro-3-hydroxybenzaldehyde, and on shaking with excess of iodine solution a di-iodo compound is obtained, bright yellow needles, m. p. 154·5°, which is probably 4 : 6-*di-iodo-2-nitro-3-hydroxybenzaldehyde*. The crude monomercurated product similarly yields an iodo compound, m. p. about 110°, probably iodo-2-nitro-3-hydroxybenzaldehyde, together with some di-iodo compound, m. p. 154·5°.

The bactericidal action of the new substances has been investigated. R. B.

Isomerism of the Oximes. XVII. Some Bromo- and Nitro-substituted Mono- and Di-methoxybenzaldoximes. O. L. Brady and L. B. Manjunath (*J. Chem. Soc.*, 1924, **125**, 1060—1068; cf. T., 1916, **109**, 650; 1920, **117**, 1040; 1923, **123**, 2434).—A continuation of previous work on the influence of negative groups on the stability of isomeric benzaldoximes. Ciusa's work (A., 1907, i, 137) on 3-nitro-*p*-methoxybenz*anti*aldoxime and its *syn*-isomeride has been confirmed. The conversion of the *anti*-isomeride into the *syn*-compound was effected by pouring a suspension of the *anti*-oxime in hydrochloric acid into sodium carbonate solution. The m. p. of the *anti*-oxime is 166° and of the *syn*-oxime 164—166°. *Acetyl-3-nitro-*p*-methoxybenz*syn*aldoxime*, colourless needles, m. p. 115°, on decomposition with sodium hydroxide yields 3-nitro-*p*-methoxybenzonitrile. The *N*-benzyl ether melts at 203° (cf. Ciusa, *loc. cit.*). The *N-methyl ether*, yellow prisms, m. p. 180°, the *O-methyl ether* of the *anti*-oxime, m. p. 120°, *carbanilino-3-nitro-*p*-methoxybenz*anti*aldoxime*, m. p. 128° (decomp.), and *carbanilino-3-nitro-*p*-methoxybenz*syn*aldoxime*, m. p. 117° (de-

comp.), are described. On hydrolysis with sodium hydroxide, the carbanilino derivative of the *anti*-oxime yields the original oxime, whereas the isomeric carbanilino derivative yields aniline and 3-nitro-*p*-methoxybenzonitrile on warming, and on prolonged boiling, ammonia and 3-nitro-*p*-methoxybenzoic acid with a little 3-nitro-*p*-methoxybenz*anti*aldoxime.

3-Bromo-*p*-methoxybenzaldehyde, obtained by bromination of *p*-methoxybenzaldehyde in acetic acid solution in the presence of iodine, readily yields 3-*bromo*-p-*methoxybenz*anti*aldoxime*, m. p. 118° (*acetyl* derivative, m. p. 82°, hydrolysed to the sodium salt of the original oxime with sodium hydroxide), which on boiling with excess of acetic anhydride is converted into 3-*bromo*-p-*methoxybenzonitrile*, m. p. 122°. The following derivatives of 3-bromo-*p*-methoxybenz*anti*aldoxime were prepared: O-*benzyl ether*, m. p. 82°; O-*methyl ether*, m. p. 76°; *phenylcarbimide* derivative, m. p. 92°, hydrolysed mainly to the original oxime, some diphenylcarbamide being also formed. The *anti*-oxime is readily converted by the hydrochloric acid method (*supra*) into 3-*bromo*-p-*methoxybenz*syn*aldoxime*, m. p. 134° [N-*benzyl ether*, m. p. 151°; N-*methyl ether*, m. p. 108°; *phenylcarbimide* derivative, m. p. 104° (decomp.), yielding ammonia and 3-bromo-*p*-methoxybenzoic acid on hydrolysis], which with cold acetic anhydride and sodium carbonate solution is converted into 3-bromo-*p*-methoxybenzonitrile. The 5-nitro-*o*-methoxybenzaldoxime, m. p. 183°, prepared by Schnell (A., 1884, 1164), is shown to be the *anti*-oxime, its *acetyl* derivative, m. p. 160°, yielding the original oxime on hydrolysis. In a similar manner, 6-nitro-3 : 4-dimethoxybenzaldoxime (A., 1900, i, 178) (*acetyl* derivative, yellow leaflets, m. p. 152°) is shown to be the *anti*-oxime. 5-Nitro-3 : 4-dimethoxybenzaldehyde, obtained from 5-nitrovanillin by methylation with diazomethane (excess of the reagent yields 5-*nitro*-3 : 4-*dimethoxyacetophenone*, m. p. 89°), or by treatment of the silver salt with methyl iodide, yields 5-*nitro*-3 : 4-*dimethoxybenz*anti*aldoxime*, m. p. 151° (*acetyl* derivative, m. p. 115°, yielding the oxime on hydrolysis). 6-Bromo-3 : 4-dimethoxybenzaldoxime (Pschorr, A., 1912, i, 775) yields an *acetyl* derivative, m. p. 140°, regenerating the original oxime on hydrolysis and accordingly has the *anti*-structure. Attempts to prepare *syn*-isomerides from 5-nitro-*o*-methoxybenz*anti*aldoxime, 6-nitro-, 6-bromo-, and 5-nitro-3 : 4-dimethoxybenz*anti*aldoximes were unsuccessful, and in all these cases solutions of the oximes in organic solvents yielded no hydrochloride on treatment with hydrogen chloride (cf. T., 1923, **123**, 1783). R. B.

Isomerism of the Oximes. XVIII. Action of Chloro-2 : 4-dinitrobenzene on some Isomeric Aldoximes. O. L. Brady and R. Truszkowski (*J. Chem. Soc.*, 1924, **125**, 1087—1096; cf. T., 1922, **121**, 2106).—Chloro-2 : 4-dinitrobenzene reacts readily in alcoholic solution with the sodium salts of substituted benz*anti*aldoximes yielding dinitrophenyl ethers, to which the *syn*-configuration is assigned (cf. Werner, A., 1894, i, 461), since on warming with alcoholic potassium hydroxide they are readily

hydrolysed with formation of sodium dinitrophenoxide and the corresponding nitrile: $R{\cdot}CH{:}N{\cdot}O{\cdot}C_6H_3(NO_2)_2 \longrightarrow RCN + (NO_2)_2C_6H_3{\cdot}OH$ (cf. T., 1923, **123**, 1190). The ethers obtained from *o*-methoxy- and *p*-hydroxy-benz*anti*aldoximes behave in this way, although previously no *syn*-derivatives of these oximes had been prepared. 3-Bromo-*p*-dimethylamino- and *o*-hydroxybenz*anti*aldoximes do not react in this way, but in the former case a dinitrophenyl ether was obtained by another method. The reaction has also been studied in the case of the sodium salts of the following *syn*-oximes: benzaldoxime, *p*-methoxybenzaldoxime, cinnamaldoxime, acetaldoxime, and heptaldoxime. A complicated reaction occurs but the only products isolated were sodium dinitrophenoxide and the corresponding aldehyde. The binary fusion curves of the *anti*-oximes and chlorodinitrobenzene indicate that in certain cases, *e.g.*, benz*anti*aldoxime and *p*-methoxybenz*anti*aldoxime, well-defined additive compounds are formed containing equimolecular quantities of the two components. *o*-Methoxy- and *o*-hydroxybenz*anti*aldoximes gave no indication of such an equimolecular compound, although in the former case there is some evidence of the formation of an unstable compound of chlorodinitrobenzene (2 mols.) and oxime (1 mol.). That stable additive compounds with chlorodinitrobenzene are characteristic of those oximes which are readily converted into *syn*-isomerides affords some support for the view that the formation of additive compounds precedes isomeric change in the oximes. 2 : 4-*Dinitrophenyl ethers* were prepared from the following: p-*methoxybenz*syn*aldoxime*, m. p. 174° (decomp.); o-*aminobenz*syn*aldoxime*, m. p. 177° (decomp.); 5-*bromo*-3 : 4-*dimethoxybenz*syn*aldoxime*, m. p. 199° (decomp.); 3 : 4-*methylenedioxybenz*syn*aldoxime*, m. p. 194° (decomp.); o-*nitrobenz*syn*aldoxime*, m. p. 184° (decomp.); p-*nitrobenz*syn*aldoxime*, m. p. 210° (decomp.); p-*dimethylaminobenz*syn*aldoxime*, m. p. 185° (decomp.); 3-*nitro*-p-*dimethylaminobenz*syn*aldoxime*, m. p. 179° (decomp.); 3 : 4-*dimethoxybenz*syn*aldoxime*, m. p. 176° (decomp.); o-*methoxybenz*syn*aldoxime*, m. p. 184° (decomp.). The *monodinitrophenyl ether* of p-*hydroxybenz*syn*aldoxime* melts at 185° (decomp.). The 2 : 4-*dinitrophenyl ether* of 3-*bromo*-p-*dimethylaminobenz*syn*aldoxime*, m. p. 181° (decomp.), was obtained by the action of sodium hydroxide solution on the powdered fusion of the *anti*-oxime (1 mol.) with chloro-2 : 4-dinitrobenzene (1 mol.). The *additive* compound of chloro-2 : 4-dinitrobenzene with benz*anti*aldoxime has m. p. 32—33°, and with *p*-methoxybenz*anti*aldoxime, m. p. 65°. R. B.

Secondary Valency of the Hydroxyl Group in Complex Salts of Protocatechualdehyde. H. Reihlein and A. Saffer. —(See ii, 384.)

Purification and Physical Constants of Acetophenone. J. L. R. Morgan and O. M. Lammert (*J. Amer. Chem. Soc.*, 1924, **46**, 881—888).—Pure acetophenone has been prepared by a method involving slow recrystallisation in the dark and in the absence of moisture, and the following constants have been determined:

freezing point 19·655°±0·002°; specific conductance k^{25} 6·43×10^{-9} mho; d_4^{25} 1·02382±0·002%. The freezing-point curve of acetophenone with small quantities of water has been determined.

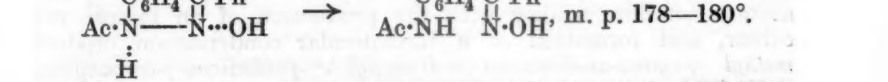
W. H.-R.

Explanation of the Catalytic Action in Friedel–Crafts' Syntheses. A. SCHAARSCHMIDT (*Z. angew. Chem.*, 1924, **37**, 286—288).—Unpublished experimental results (covered by patents) lead the author to conclude that the aluminium chloride (or ferric chloride) in a Friedel–Crafts reaction "activates" the benzene, or benzene derivative, in forming an additive compound. To

the intermediate compound formed by the three reagents he ascribes the annexed formula, in which R_1 and R_2 may be alike, as in halogenation, or unlike, as in the synthesis of acetophenone. If this compound be stable, as in the acetophenone synthesis, then a molecular proportion of aluminium chloride is needed. If it be unstable, then the aluminium chloride behaves as a true catalyst. But if one of the end-products can react with the aluminium chloride then the reaction, although really catalytic, needs for completion a molecular proportion of the agent. The presence of reactive substituent groups in the benzene derivative may likewise influence the course of the reaction.

W. A. S.

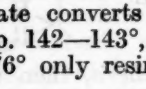
Oximes of *o*-Aminobenzophenone and the Beckmann Transformation. K. v. AUWERS and O. JORDAN (*Ber.*, 1924, **57**, [*B*], 800—808; cf. Meisenheimer and Meis, this vol., i, 433).—The configuration of the two oximes of *o*-aminobenzophenone has been deduced from their behaviour on diazotisation (A., 1893, i, 587), and is supported by the hydrolysis of 1-acetyl-3-phenylindazole with sodium hydroxide to the *N*-acetyl derivative of the *n*-oxime, m. p. 127°:



Both oximes are transformed by acetic acid saturated with hydrochloric acid into phenylindazole in approximately equal yields, the transformation being slightly quicker with the *h*-oxime, m. p. 156°. On boiling with acetic acid, the *n*-oxime yields exclusively its acetyl derivative, m. p. 178—180°, whereas the *h*-oxime is converted mainly into 1-acetyl-3-phenylindazole, a small quantity of the acetyl compound, m. p. 178—180°, being also formed. Both oximes on heating with alcohol at 160° in the presence of a trace of hydrochloric acid yield benzenylphenyleneamidine (2-phenylbenziminazole), m. p. 291° (A., 1891, 1378), but the *n*-oxime yields a purer product. A similar result was obtained with 4—5% formic acid at 140°, both oximes yielding a little *o*-aminobenzophenone and the iminazole, the *n*-oxime again giving the purer product. At 120°, the *h*-oxime was largely converted into *o*-aminobenzophenone, whereas the *n*-oxime gave mainly the iminazole. On boiling with concentrated formic acid, both oximes are converted

into the N-*formyl* derivative of the *n*-oxime, fine needles, m. p. 165°, the *h*-oxime yielding also a small quantity of 1-formyl-3-phenylindazole. The hydrochlorides of both oximes undergo the Beckmann transformation on heating, yielding the hydrochloride of 2-phenylbenziminazole, m. p. 325—328°, the transformation being more rapid and without sintering in the case of the *n*-oxime. The N-*acetyl* derivative of the *h*-oxime, m. p. 154—155°, was obtained, together with a little of the *N*-acetate, by treating the oxime in ether–pyridine solution with acetyl chloride. The N-*benzoyl* derivative of the *h*-oxime has m. p. 175—176°, and of the *n*-oxime, m. p. 201°. Both oximes on benzoylation by the Schotten-Baumann process also yield the same *dibenzoyl* compound, m. p. 165—166°, which on hydrolysis gives only the *N*-benzoate of the *n*-oxime. Treatment with methyl sulphate converts the *N*-benzoate, m. p. 201°, into its *methyl ether*, m. p. 142—143°, but from the isomeric *N*-benzoate of m. p. 175—176° only resinous products were obtained.

The great tendency to form derivatives of the *n*-oxime and the fact that both oximes give the same diacetyl and dibenzoyl compounds contrast with the behaviour of the benzildioximes, where all three series of diacyl derivatives are known. It is suggested that the *syn*-oxime has a configuration such as



comparable with those suggested for the stereoisomeric substituted diphenyl derivatives (T., 1922, **121**, 614; 1923, **123**, 2047).

R. B.

Addition Reactions of Benzoylphenylacetylene. E. P. Kohler and G. R. Barrett (*J. Amer. Chem. Soc.*, 1924, **46**, 747—753).—In the presence of a little sodium methoxide in methyl-alcoholic solution, benzoylphenylacetylene and methyl cyanoacetate combine readily with the production of an intense red colour, and formation of a termolecular condensation product *methyl γ-cyano-αε-dibenzoyl-βδ-diphenyl-Δ$^{\alpha\delta}$-pentadiene-γ-carboxylate*, CHBz:CPh·C(CN)(CO$_2$Me)·CPh:CHBz, yellow needles, m. p. 209°. Methyl α-cyanopropionate combines somewhat less readily with benzoylphenylacetylene. When one equivalent of sodium methoxide was used two products were obtained, *phenyl γ-cyano-β-phenylbutenyl ketone*, CHMe(CN)·CPh:CH·COPh, colourless prisms, m. p. 129°; and a yellow solid, from which a *substance* was obtained as greenish-yellow needles turning red at about 260°, m. p. 264°. The latter substance dissolved in boiling methyl alcohol gave, on evaporation of the solvent, sodium chloride and a yellow substance from which hot methyl alcohol extracted 4 : 6-*diphenyl*-3-*methyl*-1 : 2-*pyrone*, stout yellow needles, m. p. 113°.

In presence of a smaller quantity of the condensing agent, methyl α-cyanopropionate and benzoylphenylacetylene condense to form *methyl α-cyano-δ-keto-βδ-diphenyl-α-methyl-Δ$^{\beta}$-pentenoate*,

CHBz:CPh·C(CN)Me·CO$_2$Me,

colourless needles, m. p. 70°.

When a benzene solution of benzoylphenylacetylene was added to a suspension of the sodium derivative of benzyl cyanide, a crimson condensation *product* separated which, when decomposed with dilute hydrochloric acid, formed *phenyl γ-cyano-βγ-diphenylpropenyl ketone*, COPh·CH:CPh·CHPh·CN, colourless needles, m. p. 137°; the compound reduces permanganate in acetone, readily forms a *hydrazone*, m. p. 150—151°, and regenerates the crimson sodium compound when treated with sodium methoxide.

Equimolecular proportions of benzoylphenylacetylene and toluene-*p*-sulphinic acid, in the presence of a condensing agent, react to form *phenyl β-toluene-p-sulphonylstyryl ketone*,

$$COPh\cdot CH{:}CPh\cdot SO_2\cdot C_7H_7,$$

colourless, 6-sided plates, m. p. 141°, and smaller quantities of a *stereoisomeride* (yellow needles, m. p. 157°). The yellow compound is readily obtained from its colourless stereoisomeride, when a suspension of this in methyl alcohol is treated with a trace of sodium alkoxide. Both sulphones gave, on reduction, β-toluene-*p*-sulphonyl-β-phenylpropiophenone, and a *substance* which crystallises in fine needles, m. p. 249°. C. J. S.

Addition Reactions of certain Pentadienones. E. P. Kohler and R. W. Helmkamp (*J. Amer. Chem. Soc.*, 1924, **46**, 1018—1024). —Methyl cyanoacetate combines readily with distyryl ketone and other pentadienones in presence of sodium methoxide or hydroxide to form *cyclo*hexanone derivatives. The closing of the ring takes place much more rapidly than the addition of a second molecule of cyanoacetate. No open-chain compounds are formed as is the case with malonic and acetoacetic esters. The products do not reduce permanganate. They are extracted from ethereal solution by sodium hydrogen sulphite, and form acetals with surprising ease. The *cyclo*hexanones occur in two stereoisomeric forms; that first formed is transformed into a second, more stable to alkali, by treatment with sodium hydroxide. *Methyl* 1-*cyano*-4-*keto*-2 : 6-*diphenyl*cyclo*hexane*-1-*carboxylate*,

$$CO\begin{<}CH_2\cdot CHPh\\CH_2\cdot CHPh\end{>}C(CN)\cdot CO_2Me,$$

white filaments, m. p. 137—138°, is obtained on adding a few drops of a sodium methoxide solution to a hot saturated solution of distyryl ketone in methyl alcohol containing a little more than one equivalent of methyl cyanoacetate. Using aqueous sodium hydroxide, the isomeride is obtained in stout prisms, m. p. 146°; *oxime*, m. p. 190°; *methyl acetal*, by passing dry hydrogen chloride into a solution of the *cyclo*hexanone derivative in dry, cooled methyl alcohol, m. p. 181°. The *ethyl acetal*, m. p. 151—152°, was made as above and also by the Claisen method. The melting point may drop as low as 135—145° after standing some hours, but after one recrystallisation it is again 151—152°. Bromination gave a product containing 1—2% more bromine than required for a dibromo derivative. 1-*Cyano*-4-*keto*-2 : 6-*diphenyl*cyclo*hexane*-1-*carboxylic acid* forms needles or large, colourless prisms containing 1 mol. of acetone. On heating at 180—190°, the acetone is driven

off, followed by a mol. of carbon dioxide, giving 4-*cyano*-3 : 5-*diphenyl*cyclo*hexan*-1-*one*, minute prisms, m. p. 81—83° (decomp.); *semicarbazone*, minute prisms, m. p. 194—196° (decomp.). *Methyl* 4-*keto*-2 : 6-*diphenyl*cyclo*hexane*-1-*carboxylate*, prisms, m. p. 104·5—106°, is formed by heating the above nitrile in methyl-alcoholic hydrochloric acid. Dimethoxystyryl ketone reacts with methyl cyanoacetate in presence of a little sodium methoxide at room temperature to give a mixture of stereoisomerides of which the m. p. varies with the solvent used for crystallisation. *Methyl* 1-*cyano*-4-*keto*-2 : 6-*dianisyl*cyclo*hexane*-1-*carboxylate* is obtained as the more stable isomeride on boiling with sodium methoxide, needles, m. p. 208—209°; *methyl acetal*, m. p. 175·5—176°. Ethyl cyanoacetate condenses similarly with dimethoxystyryl ketone, and the condensation product gave the *ethyl acetal* of the above, m. p. 132—134°. A. C.

Addition Reactions of certain Pentadienones. II. Addition of Malonic Esters. E. P. KOHLER and C. S. DEWEY (*J. Amer. Chem. Soc.*, 1924, **46**, 1267—1278).—The condensation of methyl malonate with distyryl ketone in presence of bases leads to an equilibrium mixture of the three products

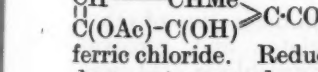
$$CHPh{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CHPh{\cdot}CH(CO_2Me)_2 \text{ (I)},$$

$CO[CH_2{\cdot}CHPh{\cdot}CH(CO_2Me)_2]_2$ (II), and *dimethyl* 4-*keto*-2 : 6-*diphenyl*cyclo*hexane*-1 : 1-*dicarboxylate* (III), from which either may be isolated by inoculation or suitable variation of conditions. Compound (III), produced in presence of sodium methoxide, forms white, irregular prisms, m. p. 135°, from which the free *acid*, $C_{20}H_{18}O_5,2H_2O$, is obtained on hydrolysis as transparent needles. The latter is stable in a vacuum, but becomes anhydrous at 75—100°, and melts at about 150° with loss of carbon dioxide and formation of the corresponding monocarboxylic acid. *Diethyl* 4-*keto*-2 : 6-*diphenyl*cyclo*hexane*-1 : 1-*dicarboxylate* forms white needles, m. p. 79°. *Dimethyl* δ-*keto*-βζ-*diphenyl*-Δ-*hexene*-αα-*dicarboxylate* (I), long, silky needles, m. p. 108°, is obtained in presence of piperidine. On oxidation with cold permanganate in acetone, it yields benzoic acid and the monomethyl ester of a tribasic acid, $C_{13}H_{14}O_6$, colourless prisms, m. p. 101°, which, by hydrolysis with potassium hydroxide and subsequent heating at 170—185°, yields carbon dioxide and phenylglutaric acid, m. p. 136°. (I) is converted quantitatively into (III) by adding it to a cold solution of sodium methoxide (5%) in methyl alcohol, but in presence of methyl malonate the compound (II) was obtained as long, silky needles, m. p. 109—112°. *Dimethyl* δ-*keto*-βζ-*diphenylhexane*-αα-*dicarboxylate*, $CH_2Ph{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CHPh{\cdot}CH(CO_2Me)_2$, m. p. 57°, is obtained by the condensation of methyl malonate with phenylethyl styryl ketone in presence of sodium methoxide. Methyl cyanoacetate condenses with distyryl ketone to form a *cyclo*hexanone derivative much more rapidly than methyl malonate. 4-*Nitro*-3 : 5-*diphenyl*cyclo*hexan*-1-*one*, obtained by the condensation of distyryl ketone and nitromethane, forms colourless, prismatic needles, m. p. 93—94°. It forms a *sodium* derivative,

from which 4-*bromo*-4-*nitro*-3 : 5-*diphenyl*cyclo*hexan*-1-*one*, small prisms, m. p. 156—157°, is obtained by the action of bromine. Styryl *p*-methoxystyryl ketone and dimethyl malonate yield a *cyclo*hexanone derivative, fine, white needles, m. p. 145—146° analogous with (III), in presence of sodium methoxide. In presence of piperidine, *dimethyl* δ-*keto*-β-*phenyl*-ζ-p-*anisyl*-Δ$^{\epsilon}$-*hexene*-αα-*dicarboxylate*, white needles, m. p. 124°, is also obtained. Styryl δ-phenylbutadienyl ketone yields similarly the *cyclo*hexanone *derivative*, $C_{24}H_{24}O_5$, lustrous, transparent prisms, m. p. 156°, and the *compound* CHPh:CH·CH:CH·CO·CH_2·CHPh·$CH(CO_2Me)_2$, white needles, m. p. 112°, which is very readily converted into the cyclic compound. Di-*p*-methoxystyryl ketone and methyl malonate yield the *cyclo*hexanone derivative, $C_{24}H_{26}O_7$, brilliant prisms, m. p. 194°, but the open-chain compound could not be isolated. *p*-Methoxystyryl δ-phenylbutadienyl ketone and di-δ-phenylbutadienyl ketone behave similarly, with formation, respectively, of *dimethyl* 4-*keto*-2-*anisyl*-6-*styryl*cyclo*hexane*-1 : 1-*dicarboxylate*, lustrous tables or prisms, m. p. 170°, and *dimethyl* 4-*keto*-2 : 6-*distyryl*cyclo*hexane*-1 : 1-*dicarboxylate*, small, lustrous prisms, m. p. 112°.

F. G. W.

Insecticides. VI. *cyclo*Pentanolone Derivatives and their Comparison with Pyrethrolone. H. Staudinger and L. Ruzicka (*Helv. Chim. Acta*, 1924, **7**, 377—390).—A number of simpler *cyclo*pentanolone derivatives have been prepared by condensing ethyl glutarate or β-methylglutarate with ethyl oxalate (Dieckmann, A., 1894, i, 324). The properties of the compounds obtained are similar in most respects to those of pyrethrolone and its derivatives (this vol., i, 523). From ethyl glutarate and ethyl oxalate, ethyl Δ$^{2\cdot4}$-*cyclo*pentadiene-3 : 4-diol-2 : 5-dicarboxylate is obtained which, by hydrolysis with 20% sulphuric acid, gives Δ^2-*cyclo*penten-3-ol-4-one, but with more dilute acid gives *ethyl*-Δ^2-cyclo*penten*-3-*ol*-4-*one*-2-*carboxylate*, m. p. 103°, b. p. 120°/1 mm. By reduction with hydrogen and palladium, the *cyclo*pentenolone gives cyclo*pentan*-3-*ol*-4-*one*, b. p. 77—78°/10 mm., which slowly forms a polymeride, m. p. 88—90°. Ethyl 1-methyl-Δ$^{2\cdot4}$-*cyclo*pentadiene-3 : 4-diol-2 : 5-dicarboxylate, m. p. 110° (cf. Dieckmann, A., 1899, i, 676), is hydrolysed by 10% sulphuric acid to *ethyl* 1-*methyl*-Δ^2-cyclo*penten*-3-*ol*-4-*one*-2-*carboxylate*, a pale yellow liquid, b. p. 103—107°/0·5 mm.; the *acetate*, a colourless oil, b. p. 95°/0·1 mm., probably has the structure



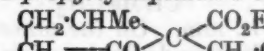
since it gives a strong reaction with ferric chloride. Reduction of the ester with hydrogen and palladium does not proceed smoothly, but some *ethyl* 1-*methyl*cyclo*pentan*-3-*ol*-4-*one*-2-*carboxylate* is obtained, a colourless oil, b. p. 104—105°/0·25 mm. (*acetate*, b. p. 104—105°/0·2 mm.), together with some 1-methyl*cyclo*pentanone. Hydrolysis of the last ester with 20% sulphuric acid gives not the expected methyl*cyclo*pentanolone, but 1-*methyl*-Δ^2-cyclo*penten*-4-*one*, colourless liquid, b. p. 57—59°/11 mm.; *semicarbazone*, m. p. 223°; p-*nitrophenylhydrazone*,

m. p. 175—176°. The *ethyl ether* of the above ester is obtained by prolonged action of boiling alcoholic sulphuric acid on the ester; it forms a colourless oil, b. p. 82—83°/0·5 mm. 1-*Methyl*-Δ^2-cyclo*penten*-3-*ol*-4-*one* (or 1-*methyl*cyclo*pentane*-3 : 4-*dione*) is obtained by hydrolysis of the above dicarboxylate with 20% sulphuric acid; it forms yellow crystals, m. p. 58—59°, b. p. 105°/21 mm., and has an odour similar to that of cresol. With *p*-nitrophenylhydrazine, it forms an *osazone*, m. p. 180°, and also gives a *benzoate*, $C_{13}H_{12}O_3$, a viscous oil, b. p. 138—140°/0·2 mm., and an *acetate*, $C_8H_{10}O_3$, b. p. 128—130°/12 mm. The *methyl ether*, $\begin{matrix}CH{-}CHMe\\ \|\\ C(OMe){-}CO\end{matrix}\!>\!CH_2$, is a colourless oil, b. p. 105—106°/15 mm. (*semicarbazone*, m. p. 192°), and the *ethyl ether* has b. p. 112—113°/10 mm. When the ethyl ether is heated at 200° with pyridine or quinoline, the ethyl group wanders from the oxygen to a carbon atom, forming a 1-*methyl*-2(5)-*ethyl*-Δ^2-cyclo*penten*-3-*ol*-4-*one*, a pale yellow oil, b. p. 112°/10 mm. 1-*Methyl*cyclo*pentan*-3-*ol*-4-*one*, obtained by reduction of the corresponding *cyclo*pentene derivative, is a colourless oil, b. p. 86°/12 mm.; it has powerful reducing properties and by auto-oxidation forms the *cyclo*pentenolone. With chrysanthemumic acid, it forms a non-insecticidal ester. The p-*nitrophenylhydrazone* has m. p. 215—216°, and the *methyl ether* is a colourless oil, b. p. 171—172°/14 mm. 1-Methyl*cyclo*pentan-3-ol-4-one forms a *polymeride*, m. p. 85—86°, which reverts on distillation to the liquid modification. 1-*Methyl*-3-*ethoxy*cyclo*pentan*-4-*one*, colourless liquid, b. p. 83—85°/12 mm., is obtained by reduction (Paal–Skita) of the corresponding methylethoxy-*cyclo*pentenone. The *acetate* of 1-methyl*cyclo*pentan-3-ol-4-one is a colourless oil, b. p. 109°/14 mm. (*semicarbazone*, m. p. 174°; p-*nitrophenylhydrazone*, m. p. 163°), and the *benzoate* has m. p. 55—56°. E. H. R.

Insecticides. VIII. Preparation of Alcohols Similar to Pyrethrolone. H. STAUDINGER and L. RUZICKA (*Helv. Chim. Acta*, 1924, **7**, 406—441).—Experiments were made to determine whether the unsaturated side-chain of pyrethrolone (1-methyl-2-pentadienyl*cyclo*pentan-4-ol-3-one, this vol., i, 523) can be replaced by other unsaturated groups without destroying the insecticidal properties of its chrysanthemumic acid ester. Methylallyl*cyclo*pentanolone (IV below) forms an insecticidal ester, weaker, however, than pyrethrine.

By the action of allyl bromide on the sodium derivative of ethyl 4-acetoxy-1-methyl*cyclo*pentan-3-one-2-carboxylate, and removal of the acetyl group with cold concentrated hydrochloric acid, was obtained *ethyl* 1-*methyl*-2-*allyl*cyclo*pentan*-4-*ol*-3-*one*-2-*carboxylate* (I) $\begin{matrix}CH_2{\cdot}CHMe\\ |\\ OH{\cdot}CH{-}CO\end{matrix}\!>\!C\!<\!\begin{matrix}CO_2Et\\ CH_2{\cdot}CH{:}CH_2\end{matrix}$, a viscous, colourless oil, b. p. 120°/1 mm.; *acetate*, b. p. 126°/1 mm. The ester is extraordinarily stable to acids; by the action of barium hydroxide it is converted into *α-hydroxy-δ-carboxy-γ-methyl-*Δ^5*-octenoic acid*,

$CH_2{:}CH{\cdot}CH_2{\cdot}CH(CO_2H){\cdot}CHMe{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2H$ (II), the *lactone* of which forms a viscous mass, b. p. 165° in a high vacuum. The *chrysanthemumcarboxylate* of (I) is a viscous oil, b. p. 180° in a vacuum, and is non-insecticidal. Reduction of the acetate of (I) by the Paal–Skita method gives *ethyl* 4-*acetoxy*-1-*methyl*-2-*propyl*cyclo*pentan*-3-*one*-2-*carboxylate*, b. p. 127°/1 mm., which is further reduced by aluminium amalgam in ether solution to *ethyl* 1-*methyl*-2-*propyl*cyclo*pentan*-3-*one*-2-*carboxylate*,



b. p. 134—136°/11 mm. (*semicarbazone*, m. p. 183°). Reduction of this with hydrogen iodide gives 1-*methyl*-2-*propyl*cyclo*pentan*-3-*one*; *semicarbazone*, m. p. 173—174°. The *ethyl ether* of (I), obtained by the action of allyl bromide on the sodium derivative of ethyl 4-ethoxy-1-methyl*cyclo*pentan-3-one-2-carboxylate, is a colourless oil, b. p. 96°/0·1 mm. The ether resists the action of acids, and by alkalis is converted into the *ethyl ether* of (II), b. p. 155—160° in a high vacuum.

Ethyl 1-methyl-Δ^4-*cyclo*penten-4-ol-3-one-2-carboxylate, in the form of its sodium or silver salt, reacts slowly with allyl bromide, forming an O-*allyl ether*, a pale yellow oil, b. p. 105°/0·5 mm., which when heated with pyridine isomerises into *ethyl* 1-*methyl*-2-*allyl*-Δ^4-cyclo*penten*-4-*ol*-3-*one*-2-*carboxylate*, b. p. 120°/0·9 mm.; by acid hydrolysis this gives 1-*methyl*-2-*propenyl*-Δ^4-cyclo*penten*-4-*ol*-3-*one* (III), m. p. 110°. The same compound is obtained by the action of allyl bromide on ethyl 1-methyl-$\Delta^{2\cdot4}$-*cyclo*pentadiene-3 : 4-diol-2 : 5-dicarboxylate, followed by decomposition of the condensation product with acid or alkali. The compound is very sensitive to atmospheric oxidation. Its *chrysanthemumcarboxylate*, a viscous oil, b. p. 165°/1 mm., is non-insecticidal. The presence of the propenyl group is proved from the formation of acetaldehyde by the decomposition of the ozonide; allyl derivatives give formaldehyde. Reduction of (III) with hyposulphite or electrolytically gives 1-*methyl*-2-*propyl*-$\Delta^{2(4)}$-cyclo*penten*-3(4)-*ol*-4(3)-*one*, crystals, m. p. 46—48°, which by further reduction gives the corresponding *cyclo*pentanolone. With bromine, (III) forms a *dibromide*, white crystals, m. p. 100—102°. Attempts to prepare a methylpropenyl-*cyclo*pentanolone by reduction of the *acetate* (b. p. 108°/0·5 mm.) and *methyl ether* (colourless oil, b. p. 127—128°/12 mm.) of (III) were unsuccessful.

By the action of allyl bromide in presence of sulphuric acid on 1-methyl-Δ^2-*cyclo*penten-3-ol-4-one, the *allyl ether* of the last is obtained, a mobile oil, b. p. 76—77°/0·75 mm., which by the action of alkalis is converted into the 2-propenyl compound, m. p. 110° (III, above), but when boiled alone gives 1-*methyl*-2-*allyl*cyclo-*pentenolone*, $\begin{matrix}CH_2{\cdot}CHMe\\ CO{-}C(OH)\end{matrix}\!\!>\!C{\cdot}CH_2{\cdot}CH{:}CH_2$, a pale yellow, mobile oil, b. p. 80—82° in a high vacuum, probably a mixture of the Δ^2- and Δ^4-isomerides. By reduction with zinc and acetic acid, this gives 1-*methyl*-2-*allyl*cyclo*pentanolone* (IV), an oil, b. p. 132

134°/14 mm., which is also probably a mixture of the two isomerides, $\begin{matrix}CH_2-CHMe\\ CO\cdot CH(OH)\end{matrix}>CH\cdot CH_2\cdot CH{:}CH_2$ and $\begin{matrix}CH_2-CHMe\\ CH(OH)\cdot CO\end{matrix}>CH\cdot CH_2\cdot CH{:}CH_2$. Its *chrysanthemumcarboxylate*, b. p. 150°/1 mm., has insecticidal properties.

The sodium derivative of 1-methyl*cyclo*pentanolone reacts with allyl bromide to form the *allyl ether*, $\begin{matrix}CH_2-\!-CO\\ CHMe\cdot CH_2\end{matrix}>CH\cdot O\cdot CH_2\cdot CH{:}CH_2$, a colourless oil, b. p. 112°/12 mm. On the other hand, the ethyl ether, when treated with sodium and allyl bromide in ether solution, gives 3-*ethoxy*-1-*methyl*-3-*allyl*cyclo*pentan*-4-*one*,

$$\begin{matrix}CH_2-\!-CO\\ CHMe\cdot CH_2\end{matrix}>C<\begin{matrix}OEt\\ CH_2\cdot CH{:}CH_2\end{matrix}'$$

a colourless oil, b. p. 110°/13 mm., which, by boiling with 20% sulphuric acid, gives 1-*methyl*-3-*allyl*-Δ^2-cyclo*penten*-4-*one*, a pale yellow oil, b. p. 112—115°/17 mm. (*semicarbazone*, crystals, decomp. 215°). When this is reduced by the Paal–Skita method, it gives 1-*methyl*-3-*propyl*cyclo*pentan*-4-*one*, a colourless oil, b. p. 82—83°/10 mm., having a faint odour of menthone; *semicarbazone*, m. p. 183°. This compound was synthesised by the action of propyl iodide on ethyl methyl*cyclo*pentanonecarboxylate prepared from ethyl β-methyladipate. Its *chrysanthemumcarboxylate*, an oil, b. p. 140—142°/0·7 mm., is not insecticidal.

Attempts to prepare methyl*cyclo*pentanolone derivatives with a geranyl side-chain were unsuccessful. 1-*Methyl*-Δ^2-cyclo*penten*-3-*ol*-4-*one geranyl ether* is a pale yellow oil, b. p. 138—142°/0·75 mm.; under no conditions does the geranyl group pass from oxygen to carbon. The *benzylidene* derivative of 1-methyl*cyclo*pentanolone is a viscous oil, b. p. 140°/1 mm. E. H. R.

Insecticides. IX. Preparation of *cyclo*Pentanolon Derivatives with Unsaturated Side Chains. H. Staudinger and L. Ruzicka (*Helv. Chim. Acta*, 1924, **7**, 442—448).—Continuing the search for substitutes for pyrethrolone (preceding abstract), a number of substituted *cyclo*pentanolones have been prepared, none of which, however, gave insecticidal esters with chrysanthemumcarboxylic acid. By boiling ethyl 1-phenyl-3 : 4-dihydroxy*cyclo*pentadiene-2 : 5-dicarboxylate with 10% sulphuric acid, 1-*phenyl*cyclo*pentenolone*, $\begin{matrix}CO-\!-CH_2\\ C(OH){:}CH\end{matrix}>CHPh$, was obtained, white crystals, m. p. 103—105°, which by reduction gave the corresponding 1-*phenyl*cyclo*pentanolone* in an impure form. *Methyl* 1-*styryl*-3 : 4-*dihydroxy*cyclo*pentadiene*-2 : 5-*dicarboxylate*, crystals, m. p. 141—142°, was obtained by condensing methyl β-styrylglutarate with methyl oxalate. By boiling 20% sulphuric acid, it is converted into 1-*styryl*-Δ^2-cyclo*penten*-3-*ol*-4-*one*, colourless crystals, m. p. 96—98°, which is reduced by zinc in sulphuric acid to 1-*styryl*-cyclo*pentan*-3-*one*, colourless crystals, m. p. 48—50°.

Crotonaldehyde condenses with ethyl malonate to give, not the expected propenylglutarate, but *ethyl* β-*methyl*-Δ^γ-*pentene*-αααε-

tetracarboxylate, a viscous oil, b. p. 174—175°/0·5 mm.; *methyl* ester, b. p. 134°/12 mm.

Ethyl *cyclo*pentan-2-one-1-carboxylate in the form of its sodium derivative condenses with allyl bromide to give *ethyl* 1-*allyl*cyclo*pentan*-2-*one*-1-*carboxylate*, a colourless oil, b. p. 125°/11 mm., which is converted by boiling 20% sulphuric acid into 1-*allyl*-cyclo*pentan*-2-*one*, a colourless oil, b. p. 86°/12 mm. (p-*nitrophenylhydrazone*, yellow crystals, m. p. 139°), which when heated with amyl formate gives a 3-*hydroxymethylene* derivative, mobile oil, b. p. 117°/11 mm. With magnesium methyl iodide, allyl-*cyclo*pentanone gives 1-*methyl*-2-*allyl*cyclo*pentan*-1-*ol*, a colourless oil, b. p. 85°/13 mm. E. H. R.

***iso*Nitriles. VII. Interaction of Phenylcarbylamine and β-Naphthol.** M. Passerini (*Gazzetta*, 1924, **54**, 184—191).—A fuller account of work already published (this vol., i, 57). The dianil derivative of 2-hydroxy-1-naphthylglyoxal has the normal molecular weight in freezing benzene; its *benzoyl* derivative, $C_{31}H_{22}O_2N_2$, forms minute, pink crystals, m. p. 163—165°, and reddens rapidly in the air. 2-Hydroxy-1-naphthylglyoxal diphenylhydrazone, $OH\cdot C_{10}H_6\cdot C(:N\cdot NHPh)\cdot CH:N\cdot NHPh$, has m. p. 240° (decomp.). The *lactone* of 2-*hydroxy*-1-*naphthylglyoxylic acid* (*loc. cit.*), forms yellow needles, m. p. 184—185°, has an acid reaction towards indicators, and gives an intense red coloration with concentrated sulphuric acid. The *barium* salt of the corresponding acid has been prepared. T. H. P.

3 : 3 : 5 : 6-Tetrachloro- and -Tetrabromo-1 : 2 : 4-triketo*cyclo*hexenes. T. Zincke and E. Weishaupt (*Annalen*, 1924, **437**, 86—105).—The two compounds, $C_6H_4O_8N_2Cl_4$ and $C_6H_4O_5Cl_4$, obtained from tetrachloro-*o*-benzoquinone (Zincke, this vol., i, 163) have now been prepared by treating tetrachloropyrocatechol with fuming nitric acid containing 10% of sulphuric acid. Tetrabromopyrocatechol yields analogous compounds. The compound, $C_6H_4O_5Cl_4$, is shown to be 3 : 3 : 5 : 6-*tetrachloro*-1 : 2 : 4-*triketo*cyclo*hexene dihydrate*, $CO<\begin{matrix}CCl=CCl\\CCl_2\cdot C(OH)_2\end{matrix}>C(OH)_2$. It is also obtained by chlorinating (and simultaneously hydrolysing) triacetylhydroxyquinol and forms pale yellow needles, m. p. 96°. When reduced it yields 3 : 5 : 6-trichloro-1 : 2 : 4-trihydroxybenzene (Zincke and Schaum, A., 1894, i, 231) and when heated at 120—125°, or with water or dilute acid decomposes giving trichlorohydroxybenzoquinone (Zincke and Schaum, *loc. cit.*) and a compound, $C_5O_2Cl_4$, probably 1 : 2 : 4 : 4-*tetrachloro*-3 : 5-*diketo*cyclo*pentene*. The latter was the sole product when the triketo compound was treated with calcium hypobromite. It is a steam-volatile substance with a quinone-like odour, forming broad needles, m. p. 65°, giving an *anilide*, $C_5O_2Cl_3\cdot NHPh$, yellow needles, m. p. 165°, and with *o*-phenylenediamine a *eurhodol*, $C_5(OH)Cl_3{:}N_2C_6H_4$, yellow needles, strongly fluorescent in alcoholic solution. Similarly, 3 : 3 : 5 : 6-*tetrabromo*-1 : 2 : 4-*triketo*cyclo*hexene*, pale yellow prisms or tables, m. p. 83—84°, was obtained (together with the compound $C_6H_4O_8N_2Br_4$)

by treating tetrabromopyrocatechol with the mixed acid. When reduced, it gives 3 : 5 : 6-tribromo-1 : 2 : 4-trihydroxybenzene (Thiele and Jaeger, A., 1901, i, 701), and decomposes like the chloro-compound but more readily, yielding tribromohydroxybenzoquinone, and 1 : 2 : 4 : 4-*tetrabromo*-3 : 5-*diketo*cyclo*pentene*, pale yellow prisms, m. p. 142—143°; *anilide*, yellow needles, m. p. 182°; *eurhodol*, yellow needles, darkening but not melting at 170° and giving a strongly fluorescent solution. This diketone treated with sodium hypobromite gives bromoform and dibromomaleic acid (cf. Pfeiffer and Böttler, A., 1919, i, 62); with 80% alcohol at 100° it is converted into 2 : 4 : 4-*tribromo*-3 : 5-*diketo*cyclo*pentenol*, a crystalline powder, m. p. 196° (decomp.), reconverted into the parent substance by phosphorus pentabromide; the corresponding *methoxy* (leaflets, m. p. 89—90°) and *ethoxy* (pale yellow needles, m. p. 111—112°) compounds are obtained when anhydrous alcohols are used and are hydrolysed to the hydroxy derivative by heating with dilute alcohol. W. A. S.

Studies in the Anthracene Series. VIII. E. de B. Barnett and M. A. Matthews (*J. Chem. Soc.*, 1924, **125**, 1079—1083; cf. Battegay, A., 1923, i, 1103, 1104).—The anthraquinonesulphonic acids on reduction with iron and hydrochloric acid are readily converted into the corresponding anthronesulphonic acids, from which the dianthronesulphonic acids are obtained by oxidation with sodium peroxide. The following *sodium* and *aniline anthrone*- and *dianthrone-sulphonates* are described: 9-(or 10-)anthrone-1-sulphonate; -2-sulphonate; -1 : 5-disulphonate; and -1 : 8-disulphonate; dianthrone-ββ′-disulphonate, -1 : 5 : 1′ : 5′-tetrasulphonate, and -ααα′α′-tetrasulphonate. The aniline salts have no definite melting points (cf. A., 1923, i, 234). The change of colour of the anthrone-1 : 8-disulphonic acid on the addition of alkali is sufficiently sharp for use as an indicator. On reduction with aqueous sodium sulphide, the anthraquinonesulphonic acids are reduced to the corresponding anthraquinolsulphonic acids and in consequence act as catalysts in reduction reactions with sodium sulphide. The additive compounds of the anthracenemonosulphonic acids with nitric acid are too unstable to be isolated, but on treatment with pyridine are converted into the corresponding nitroanthracene-sulphonic acids. 9-(or 10-)*Nitroanthracene*-1-*sulphonic acid*, yellow needles, and 9-(or 10-)*nitroanthracene*-2-*sulphonic acid* were prepared, but no nitro compound could be obtained from anthracene-1 : 5- or -1 : 8-disulphonic acid. Anthracene-2-sulphonic acid does not give an aniline salt under the usual conditions, but the following well crystallised salts were prepared: *aniline anthracene*-1-*sulphonate*, *aniline anthracene*-1 : 5-*disulphonate*, *aniline anthracene*-1 : 8-*disulphonate*. R. B.

Trihydroxymethylanthraquinones. III. Synthesis of Emodin. R. A. Jacobson and R. Adams (*J. Amer. Chem. Soc.*, 1924, **46**, 1312—1316).—3 : 5-Dimethoxy-2-(2′-hydroxy-4′-methylbenzoyl)benzoic acid was treated with bromine in glacial acetic acid with formation of the 5′-*bromo* derivative, thick, white needles,

m. p. 258—259°. On heating with fuming sulphuric acid and boric acid and diluting, *4-bromo-1-hydroxy-6 : 8-dimethoxy-3-methylanthraquinone*, orange-red needles, m. p. 208—209°, was obtained. This yielded 1 : 6 : 8-trihydroxy-3-methylanthranol (emodin anthranol) on reduction with hydriodic acid in glacial acetic acid, from which 1 : 6 : 8-trihydroxy-3-methylanthraquinone, identical with natural emodin, was obtained on oxidation with chromic oxide in glacial acetic acid. F. G. W.

Camphanylcarbinol. H. Rupe and J. Brin (*Helv. Chim. Acta*, 1924, **7**, 546—556).—Bornylenecarboxylic acid was obtained by heating borneolcarboxylic acid with acetic anhydride (cf. Bredt, A., 1909, i, 499). The *chloride* has b. p. 110°/11 mm.; *ethyl* ester, b. p. 114—115°/10 mm.; *phenyl* ester, rhombic crystals, m. p. 63—64°. By electrolytic reduction of the potassium salt, camphanecarboxylic acid was obtained; *chloride*, b. p. 110°/12 mm.; *ethyl* ester, b. p. 113°/11 mm.; *phenyl* ester, long prisms, m. p. 41°. *Camphanylcarbinol* (*hydroxymethylcamphane*),

$$C_8H_{14}\begin{cases}CH\cdot CH_2\cdot OH\\ |\\ CH_2\end{cases},$$

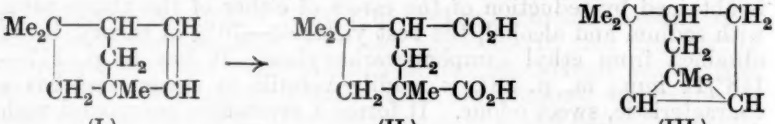
is obtained by reduction of the esters of either of the above acids with sodium and alcohol, the best yield, 65—70% of theory, being obtained from ethyl camphanecarboxylate. It has b. p. 117—118°/11 mm., m. p. 28°, is readily volatile in steam, and has a characteristic, sweet odour. It forms a crystalline compound with calcium chloride, which serves for its purification. The *formate* is a mobile liquid, b. p. 110°/11 mm.; *acetate*, b. p. 120°/11 mm.; *benzoate*, b. p. 195°/12 mm.; p-*nitrobenzoate*, long, white needles, m. p. 99—100°; p-*aminobenzoate*, glistening leaflets. The carbinol is dehydrated much less readily than camphylcarbinol (A., 1919, i, 29), but when heated with phosphoric acid is converted into *methylenecamphane*, $C_8H_{14}\begin{cases}CH{:}CH_2\\ |\\ CH_2\end{cases}$, a mobile oil with a strong, unpleasant odour, b. p. 58—62°/11 mm. The constitution of this compound is proved by the formation from it of *bromomethylcamphane*, b. p. 105—108°/12 mm., d_4^{20} 1·1948, $[\alpha]_D^{20}$ 11·57°, which is also obtained by the action of hydrogen bromide and acetic acid on the carbinol. The bromo compound reacts with aniline to give *phenylcamphanylcarbinylamine*, $C_8H_{14}\begin{cases}CH\cdot CH_2\cdot NHPh\\ |\\ CH_2\end{cases}$, b. p. 190—193°/11 mm.; p-*tolylcamphanylcarbinylamine* forms white, silky needles, m. p. 61—62°. The bromo compound does not form a compound with magnesium, but is converted into *dicamphanylethane*, a viscous oil, b. p. 205—208°/11 mm. E. H. R.

The Rotation Dispersion of Camphor. F. Bürki (*Helv. Chim. Acta*, 1924, **7**, 537—540).—Measurements of the rotation dispersion of camphor made by Rupe (A., 1915, ii, 717) and Gumprich (*Physikal. Z.*, 1923, **24**, 434) are compared by calculating Rupe's characteristic wave-length, λ_a, the λ_0 of Lowry and Dickson, and Rupe's product, $\lambda_0 . \lambda_a$. The rotation-dispersion in benzene

is slightly anomalous, and it is recommended to use alcohol when possible for such measurements. E. H. R.

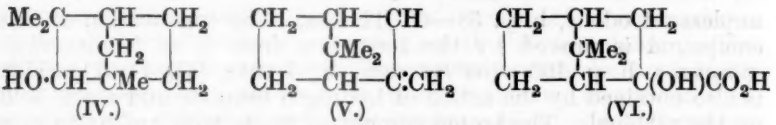
Probable Presence of Thujone in the Essential Oil of *Artemisia Herba Alba*. E. ALINARI (*Annali Chim. Appl.*, 1924, **14**, 109—112).—This oil, d^{15} 0·9257, α_D^{18} +3·88°, n_D^{20} 1·4653, contains 14·4% of free, and 7·39% of combined alcohols, calculated as $C_{10}H_8O$. The presence of camphor has been demonstrated and that of thujone is probable (cf. Grimal, A., 1904, ii, 605; also *B.*, 1924, 536). T. H. P.

The Xanthate Method in the Fenchone and *iso*Fenchone Series. S. NAMETKIN (*J. pr. Chem.*, 1923, ii, **106**, 25—38).—Assuming Semmler's formulæ for fenchone and *iso*fenchone, the elimination of water in the normal (1 : 2) position is only possible with *iso*fenchyl alcohol, and the hydrocarbon obtained should be analogous to bornylene. This is substantiated by the fact that fenchylene (I), obtained by the decomposition of *iso*fenchyl xanthate, on oxidation with potassium permanganate is converted into fenchocamphoric acid (II).



(I.) (II.) (III.)

The dehydration of *iso*fenchyl alcohol takes place also in the 1 : 3 position, leading to the formation of the isomeric *cyclo*fenchene (III). On the other hand, fenchyl alcohol (IV) cannot eliminate the elements of water in the 1 : 2 position and, as might be expected, by dehydration gives the same *cyclo*fenchene. dl-*Fenchene* (V) is also produced in the reaction, giving *dl*-hydroxyfenchenic acid (VI) by oxidation with potassium permanganate.



(IV.) (V.) (VI.)

[With A. SELIVANOV.]—*dl*-Fenchene was prepared by the dehydration of crude fenchyl alcohol with phthalic acid. The fraction, b. p. 194—199°, heated with phthalic anhydride at 170°, forms a crystalline *hydrogen phthalate* which was converted into *sodium fenchyl phthalate*, m. p. 146·5°, $[\alpha]_D$ +23·23°. On hydrolysis with alcoholic potassium hydroxide it yields pure fenchyl alcohol, b. p. 200—200·5°/750 mm., m. p. 49°, $[\alpha]_D$ −10·9°. Its steric configuration corresponds with that of borneol as shown by its stability towards the dehydrating action of phthalic acid. The stereoisomeride corresponding with *iso*borneol is probably liquid and, on account of its ready elimination of water, cannot be present in the crystalline alcohol. *cyclo*Fenchene, $C_{10}H_{16}$, is obtained by heating ethyl fenchylxanthate at 150—170°, finally raising the

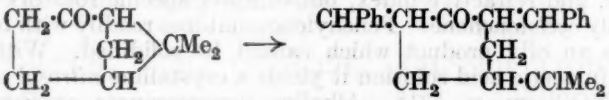
temperature to 230°. The crude product was left with 1½% potassium permanganate solution for some time, the excess of oxidant removed, and the hydrocarbon distilled three times over sodium. It was identical with Aschan's *cyclo*fenchene (β-pinolene); b. p. 143—143·5°/747·5 mm., d_4^{20} 0·8609, n_D^{20} 1·4532, $[\alpha]_D$ −1·77° (cf. A., 1912, i, 198). The hydration of *cyclo*fenchene yields a product which on oxidation is converted into *cis*-fenchocamphoric acid and would thus seem to be *iso*fenchyl alcohol, since oxidation of this alcohol has been shown to give the same product. An oily product unattacked by permanganate is also found among the products of hydration. The oxidation product obtained from the crude fenchenes by potassium permanganate contains *dl*-hydroxyfenchenic acid, m. p. 154—155°, $[\alpha]_D$ −37·42° in ether, proving definitely the presence of the *dl*-fenchene in the crude fenchene.

[With A. RUSCHENTZEFF.]—Crude *iso*fenchyl alcohol is obtained by hydration of *dl*-fenchene. It was purified by conversion into the xanthate from which, by the action of alcoholic ammonia, the *xanthamide* was obtained, needles, m. p. 69—70°, $[\alpha]_D$ −37·77° in alcohol. Hydrolysis of the amide by alcoholic alkali gives pure *iso*fenchyl alcohol, m. p. 60·5—61°, $[\alpha]_D$ −27·04° in alcohol. Fenchylene is obtained by heating methyl *iso*fenchylxanthate, its amide, or the liquid *iso*fenchylxanthamide which probably contains a mixture of esters, at 160—180°. The products obtained gave the following constants: (i) from the ester, b. p. 139—140°/760 mm.; d_4^{20} 0·8381; n^{20} 1·4494; $[\alpha]_D$ −68·76° in alcohol; (ii) from the solid amide, b. p. 140—141°/740 mm.; d_4^{20} 0·8397; n^{20} 1·4502; $[\alpha]_D$ −57·28° in alcohol; (iii) from the liquid amide, b. p. 140·5—141·5°/740 mm.; d_4^{20} 0·8398; n^{20} 1·4505; $[\alpha]_D$ −50·98°. Fenchylene has the lowest boiling point of all the hydrocarbons of formula $C_{10}H_{16}$; it differs also from *cyclo*fenchene and fenchene in its lower specific gravity and refractive index. The differences between the three preparations of fenchylene are probably due to the presence of varying amounts of a hydrocarbon of higher boiling point, specific gravity, and refractive index, but of lower specific rotatory power, probably *cyclo*fenchene. Fenchylene combines readily with bromine to give an oily product which cannot be solidified. With ethyl nitrite in acetic acid solution it yields a crystalline *nitrosyl chloride*, $C_{10}H_{16}NOCl$, m. p. 131°. Alkaline permanganate oxidises it to *cis*-fenchocamphoric acid. F. G. P.

Pinene. V. Preparation of α- and δ-Pinene. L. RUZICKA and S. PONTALTI (*Helv. Chim. Acta*, 1924, **7**, 489—495).—To complete the partial synthesis of *dl*-α-pinene, of which two stages have already been described (Ruzicka and Trebler, A., 1921, i, 36, 796), it was necessary to establish the genetic relationship between pinocamphone and pinocamphylamine. The latter was therefore prepared from pinocamphone by Wallach's method (A., 1901, i, 90) and methylated to pinocamphyltrimethylammonium iodide, m. p. 231°. The m. p. of this compound differs from that of previous preparations of Ruzicka and Trebler (m. p. 255°), and is probably a different mixture of *cis*- and *trans*-isomerides. When

the pinocamphyltrimethylammonium hydroxide was distilled in a high vacuum it gave pinocamphyldimethylamine (which when treated with methyl iodide gave the parent substance with unchanged m. p., 231°) and a hydrocarbon. The latter when oxidised gave a mixture of pinonic acid, proving the presence of α-pinene, and an acid, m. p. 186—187°, identical with that obtained by Wallach (A., 1906, i, 683) by oxidation of *dl*-pinocamphone. This acid, for which the name pinocamphoric acid is proposed, must have the formula, $CH<^{CH\cdot CHMe\cdot CO_2H}_{CH\cdot CO_2H}>CMe_2$, and proves the presence of δ-pinene (cf. Blumann and Zeitschel, A., 1921, i, 426). The dicarboxylic acid, m. p. 192°, obtained by Gildemeister and Köhler (A., 1910, i, 180) by oxidising a hydrocarbon obtained by the decomposition of *l*-pinocamphyl xanthate prepared from pinocamphone from hyssop oil, is shown to be identical with pinocamphoric acid. *l*-Pinocamphone was converted by the above reactions into a mixture of α- and δ-pinene, giving a mixture of pinonic and pinocamphoric acid (m. p. 192°) on oxidation. The dihydroverbenene of Blumann and Zeitschel (*loc. cit.*) is probably not δ-pinene, but contains an active form of α-pinene. E. H. R.

Terpenes and Ethereal Oils. CXXVIII. Condensation of Intracyclic Ketones with Two Mols. of Aromatic Aldehydes. O. Wallach (*Annalen*, 1924, **437**, 187—189; cf. A., 1899, i, 532).—Dicyclic ketones having a methylene group adjacent to the carbonyl group and in which by rupture of the bridge linkings a second methylene group vicinal to the carbonyl can be formed, condense with aromatic aldehydes in the presence of hydrochloric acid, yielding chlorodibenzylidene compounds. Thus nopinone and benzaldehyde yield 3 : 5-*dibenzylidene*-α-*chloro*isopropylcyclo*hexan*-4-*one*, yellow needles, m. p. 148—149°, the bridge ring being first ruptured by addition of hydrogen chloride, followed by condensation with two molecules of aldehyde:



In the presence of alkali, nopinone and benzaldehyde yield the monobenzylidene derivative, m. p. 106° (cf. A., 1901, i, 89), which with benzaldehyde and hydrochloric acid in alcoholic solution yields the dibenzylidene derivative. Similarly, verbanone yields a *chlorodibenzylidene* derivative, $C_{24}H_{25}OCl$, m. p. 143°, and sabina ketone a *chlorodibenzylidene* derivative, $C_{23}H_{25}OCl$, m. p. 157°, and with anisaldehyde a condensation *product*, m. p. 198°. R. B.

Terpenes and Ethereal Oils. CXXIX. Review of the Boiling Points of Stereoisomeric Modifications of Alicyclic Compounds. O. Wallach (*Annalen*, 1924, **437**, 190—194; cf. A., 1893, i, 274; 1898, i, 485; 1913, i, 482; 1915, i, 423).—The boiling points of *l*- and *d*-menthone as given by various authors fluctuate between 204° and 210°. A careful redetermination under exactly

comparable conditions gives the b. p. 210—210·25° for *l*-menthone and 210·5° for *dl*-menthone. Attempts to determine the boiling points of the different menthonoximes gave no satisfactory results, and it is doubtful whether stereoisomeric compounds can be distinguished from one another by their boiling points. The semi carbazone (m. p. 209°) from trimethyl*cyclo*pentanone (A., 1915, i, 499) was separated by crystallisation into two fractions, m. p. 178° and 214°, which on decomposition with oxalic acid yield *ketones*, b. p. 162—168°, and 167—171°, giving *oximes*, m. p. 78° and 110°, respectively. The original trimethyl*cyclo*pentanone (b. p. 164—167°, oxime, m. p. 105°) is evidently a mixture, but it was not possible to decide from these results whether the isomerism was purely physical, or chemical through the formation of the two theoretically possible isomerides, 1 : 1 : 2-trimethyl*cyclo*pentan-4-one and 1 : 1 : 4-trimethyl*cyclo*pentan-2-one. R. B.

Essential Oils from *Leptospermum Liversidgei*. A. R. Penfold (*J. Roy. Soc. New South Wales*, 1922, **56**, 82—87).—There appear to be two, and probably three, distinct forms of this shrub, yielding, respectively, 0·25—0·3% of oil with 35—50% of citral (no citronellal; cf. Baker and Smith, *ibid.*, 1905, **39**, 124), about 0·55% of oil containing 70—80% of citronellal (no citral), and about 0·6—0·8% of oil containing about 70—80% of citral (no citronellal?). W. T. K. B.

A New Stearopten occurring in some Essential Oils of the *Myrtaceæ*. A. R. Penfold and F. R. Morrison (*J. Roy. Soc. New South Wales*, 1922, **56**, 87—89).—The essential oils of *Bœckea crenulata* and *Darwinia grandiflora* contain 5·5% and 2%, respectively, of a solid crystallising from alcohol in primrose-yellow needles or monoclinic prisms, m. p. 103—104°. Its solution in alcohol is optically inactive. The compound appears to have the formula $C_{13}H_{18}O_4$, and to contain two methoxy groups; it is considered to be a phenol ether. W. T. K. B.

Miscibility Test for Eucalyptus Oils. C. E. Fawsitt and C. H. Fischer (*J. Roy. Soc. New South Wales*, 1922, **56**, 109—114).—The determination of the critical solution temperature by mixing the oil in definite proportions with a suitable liquid (*e.g.*, aqueous alcohol) giving two layers at the ordinary temperature, heating until only one layer is formed, and then allowing to cool until a cloudiness develops, affords a more sensitive test than the method in which the volume of aqueous alcohol required for complete solution of one volume of the oil is determined. [Cf. *B.*, 1924, 536.] W. T. K. B.

Australian *Melaleucas* and their Essential Oils. VI. R. T. Baker and H. G. Smith (*J. Roy. Soc. New South Wales*, 1922, **56**, 115—124).—The oil from *Melaleuca ericifolia* (yield 0·84%) differs from oil of cajuput, by having a lower sp. gr. (d^{15} 0·8938), by the terpenes being strongly dextrorotatory, by containing *d*-terpineol in some quantity, by containing considerably less cineol, and by the principal oxygenated constituent being terpineol and not

cineol. It has $[\alpha]_D$ +13·3°, n^{20} 1·4705, and saponification value 6·96. The oil obtained from young growths of *M. Deanei* (yield 0·7%) consists mainly of *d*-pinene, with only a small amount of oxygenated substances. The crude oil has d^{15} 0·8888, $[\alpha]_D$ +22·7°, n^{22} 1·4646, and saponification value 5·7. W. T. K. B.

Essential Oil of *Backhousia myrtifolia* [Grey or "Scrub" Myrtle]. I. A. R. PENFOLD (*J. Roy. Soc. New South Wales*, 1922, **56**, 125—129).—When the leaves and terminal branchlets of this tree are distilled with steam a brownish-yellow oil of pleasing odour and d^{15} 1·026—1·057 is obtained in an average yield of 0·42%, this being greatest in spring. The oil contains 75—80% of the rare phenol ether elemicin, together with pinene, a paraffin (m. p. 62—63°), a sesquiterpene, b. p. 120—138°/10 mm., an alcohol, b. p. 95—109°/10 mm., d^{15} 0·9018, rotation +7·6°, n^{20} 1·4770, and a phenol (0·24—0·5%). W. T. K. B.

Oak Moss Oil. H. WALBAUM and A. ROSENTHAL (*Ber.*, 1924, **57**, [*B*], 770—773).—The odoriferous substance obtained by extraction or steam distillation of oak moss has been identified as orcinol monomethyl ether. The oil also contains ethyl β-orcinolcarboxylate (methyl 2 : 4-dihydroxy-3 : 6-dimethylbenzoate), m. p. 142°. By extracting the lichen with alcohol, ethyl everninate (6-hydroxy-4-methoxy-2-methylbenzoate), m. p. 76°, was isolated, but it is probable that the free acid occurs in the lichen and is esterified by the alcohol. Everninic acid may be the parent substance of the monomethyl orcinol. R. B.

Refractive Index of Caoutchouc. D. F. TWISS (*Nature*, 1924, **113**, 822).—Caoutchouc has n_D^{15} 1·525. A. A. E.

The African Poison, Acocantherine. J. MOIR (*J. S. Afr. Chem. Inst.*, 1924, **7**, 28—33).—Acocantherine, prepared from *Acokanthera venenata*, dissolves in concentrated sulphuric acid yielding an orange-yellow solution showing an absorption band at λ 476; after some time the colour darkens, a green fluorescence develops, and a band appears at λ 495. When hydrolysed with 2% sulphuric acid it yields rhamnose and acocanthic acid lactone; the latter gives a fluorescent orange-coloured solution in concentrated sulphuric acid with a band at λ 470, and a yellow solution in sodium hydroxide solution with a band at λ 440. Acocantherine therefore resembles ouabaine, and there is but little difference between the properties of acocanthic acid and those of the synthetic substance *benzoumbelliferone* (2 : 4-*dihydroxydiphenyl*-2′-*carboxylic acid lactone*). W. P. S.

Insecticides. X. Synthesis of Pyrethrines. H. STAUDINGER and L. RUZICKA (*Helv. Chim. Acta*, 1924, **7**, 448—458).—Both active constituents of insect powder (this vol., i, 700) have been synthesised from their acid and alcoholic components, but the synthesis is incomplete, as synthetic chrysanthemumic acid has not yet been resolved and pyrethrolone has not been completely synthesised (cf. i, 522). Pyrethrine I, from chrysanthemumcarb-

oxylic chloride and pyrethrolone in presence of pyridine, is a colourless, viscous oil, b. p. 145—150°/0·125 mm., $[\alpha]_D^{18}$ −16·2°; the semicarbazone is crystalline, but melts indefinitely between 80° and 90°. Pyrethrine II, obtained similarly from the chloride of methyl hydrogen chrysanthemumdicarboxylate, is a colourless, odourless, viscous oil, b. p. 195°/0·167 mm.; its semicarbazone is amorphous. A large number of esters of pyrethrolone with organic acids and of chrysanthemumcarboxylic acids with alcohols of many types were prepared, but none of these had insecticidal properties at all comparable with those of the pyrethrines. E. H. R.

Furoyl Peroxide. H. Gelissen and J. D. van Roon (*Rec. trav. chim.*, 1924, **43**, 359—366).—*Furoyl peroxide*, $(C_4H_3O\cdot CO)_2O_2$, white crystals, m. p. 86°, which turn yellow in the air, is prepared by the action of cold alkaline hydrogen peroxide on pyromucyl chloride. It is less stable than benzoyl peroxide, is hydrolysed by water, and liberates iodine from potassium iodide solution. It is also more sensitive to shock than benzoyl peroxide, and explodes without smoke. Diphenyl can be obtained by warming benzoyl peroxide in benzene solution, but difuryl is not analogously formed from furoyl peroxide. E. H. R.

Trimethylene Trisulphides. O. Hinsberg (*Ber.*, 1924, **57**, [*B*], 836—838; cf. A., 1914, i, 185, 797; 1923, i, 1056).—The sulphoxide obtained by the action of hydrogen peroxide on trimethylene trisulphide $(CH_2S)_3$, is smoothly oxidised by permanganate in faintly acid solution to yield trimethylene trisulphone, $(CH_2SO_2)_3$ (cf. Fromm and Schultis, A., 1923, i, 580). The sulphoxide must therefore be the trimeric form, $(CH_2SO)_3$. Since hydriodic acid converts it into the trisulphide of m. p. 247°, and since it is re-formed from the latter by oxidation with hydrogen peroxide, this trisulphide must be trimeric, and stereoisomeric with that of m. p. 216°. Possibly the crude trisulphide forms a third stereoisomeride which changes into the 216° form on crystallisation. F. A. M.

Synthesis of Cyclic Polysulphides. I. Sir P. C. Rây (*J. Chem. Soc.*, 1924, **125**, 1141—1144).—When dithioethylene glycol (2 mols.) and benzylidene chloride (1 mol.) are boiled together gently during 30 hours, the chief products are *benzylidenediethylene tetrasulphide*, $CHPh<^{S\cdot C_2H_4\cdot S}_{S\cdot C_2H_4\cdot S}$, and *trisulphide*, $CHPh<^{S\cdot C_2H_4}_{S\cdot C_2H_4}>S$, both of which are oily liquids; diethylene di- and tri-sulphides are also formed as by-products. According to the duration of heating, benzylidenediethylene trisulphide reacts with boiling methyl iodide to form *methiodides* approximating in composition to $C_4H_8S_2,2MeI$ and $C_4H_8S,3MeI$; with ethyl iodide it forms an *ethiodide*, $2C_{11}H_{14}S_2,EtI$, together with diethylene di- and tri-sulphides.

With mercuric chloride and platinic chloride, benzylidenediethylene tri- and tetra-sulphides form additive compounds; in the

substances formed from platinic chloride, the valency of platinum may vary (cf. T., 1923, **123**, 133).

Oxidation of benzylidenediethylene trisulphide with nitric acid yields benzoic acid, ethanedisulphonic acid, and sulphuric acid.

C. J. S.

Strychnine and Brucine. R. Ciusa and G. Scagliarini (*Gazzetta*, 1924, **54**, 202—203).—The authors reply to Oliveri-Mandalà and Comella (A., 1923, i, 1223) on certain points concerning the structure of *iso*strychnine. T. H. P.

[Partial] Synthesis of 2-*n*-Butylpyrrolidine. E. E. Blaise and A. Cornillot (*Compt. rend.*, 1924, **178**, 1186—1188; cf. Blaise and Houillon, A., 1906, i, 692, also following abstract).—Magnesium *n*-butyl iodide converts ethyl cyanoacetate into *ethyl* n-*valerylacetate*, b. p. 112°/18 mm., converted by semicarbazide and phenylhydrazine into the *carbamylpyrazolone*, m. p. 165°, and *butylphenylpyrazolone*, m. p. 79°, respectively. The potassium derivative of the valeryl ester reacts with β-iodoethylphthalimide to give a compound which when hydrolysed with hydrobromic acid affords 2-n-*butylpyrroline*, b. p. 68·5°/19 mm. [*chloroplatinate*, m. p. 182—183° (decomp.)]. The hydrochloride reacts with potassium cyanate, yielding the *carbamide*, $C_9H_{16}ON_2,H_2O$, m. p. 104—105°. Hydrogenation of the base has not yet been effected. H. J. E.

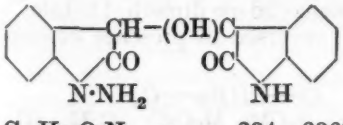
Synthesis of 2-*n*-Butylpyrrolidine. E. E. Blaise and A. Cornillot (*Compt. rend.*, 1924, **178**, 1617—1619).—2 : 5-Dimethylpyrroline, obtained by reducing the product of the interaction of ammonia and acetonylacetone, forms a chloroaurate, m. p. 77° [Knorr and Rabe (A., 1902, i, 54) gave 68—69°], and a phenylcarbamide, m. p. 130°. When reduced in an atmosphere of hydrogen and in presence of platinum chloride previously reduced by means of gum arabic, it yields 2 : 5-dimethylpyrrolidine as a colourless liquid, b. p. 106·5°; the chloroaurate has m. p. 85° [Fenner and Tafel (A., 1900, i, 111) gave 96—100°] and the phenylcarbamide, m. p. 142°. 2-*n*-Butylpyrrolidine, similarly prepared from 2-*n*-butylpyrroline, agrees exactly with the compound previously obtained by Blaise and Houillon (A., 1906, i, 692), so that Hess' compound (A., 1920, i, 85) must have another constitution. It is suggested that the use of hydriodic acid as a reducing agent should be avoided in all synthetic processes used for the determination of constitution. T. H. P.

Nitropyrrole and Pyrrole-aldehydes. A. Angeli (*Ber.*, 1924, **57**, [*B*], 834—836).—A criticism of recent work by Fischer, Zerweck, and Smeykal (A., 1922, i, 758; this vol., i, 201); their statement that alkylated pyrroles can be nitrated smoothly is not strictly accurate, as they worked with carboxylic esters of pyrrole-ketones and -aldehydes, dicarboxylic esters, etc. Angeli had already shown that pyrrole, but not methyl pyrryl ketone, is rapidly oxidised by permanganate. Fischer and Zerweck overlooked Angeli's synthesis of pyrrole-aldehydes using formic ester

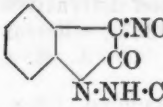
and sodium alkoxide, which favours a hydroxymethylene structure for these substances (cf. A., 1915, i, 454; and Fischer, A., 1913, i, 1225). Pyrrole-aldehyde and its di-ortho substituted derivatives do not respond to Baudisch's reagent (A., 1921, ii, 337), whereas 1-methylpyrrole-aldehyde does. F. A. M.

1-Amino-oxindole. P. W. Neber and H. Keppler (*Ber.*, 1924, **57**, [*B*], 778—787).—1-Amino-oxindole (A., 1922, i, 546) on treatment with 1 or 2 mols. of benzaldehyde yielded 1-*amino*-3-*benzylideneoxindole* (pale yellow crystals, m. p. 116°) or 1-*benzylideneamino*-3-*benzylideneoxindole* (yellow needles, m. p. 161°), respectively. The monobenzylidene compound with amyl nitrite and hydrochloric acid gave 3-benzylideneoxindole, m. p. 172° (cf. Wahl and Bagard, A., 1909, i, 735). With the three nitrobenzaldehydes the products were the 1-nitrobenzylideneaminooxindoles, which were conveniently prepared from the corresponding nitrobenzylidenephenylhydrazine-*o*-acetic acids. N'[*o-Nitrobenzylidene*]-*phenylhydrazine*-o-*acetic acid* forms orange needles, m. p. 158°; the *meta* compound forms orange leaflets, m. p. 166°, the *para* compound scarlet needles, m. p. 175°; boiling glacial acetic acid converts the acids into the corresponding 1-*nitrobenzylideneamino-oxindoles*, which form yellow needles, *ortho*, m. p. 168—170°; *meta*, m. p. 160°; *para*, m. p. 220—227°. These are stable to mineral acids and insoluble in alkalis. The *o*-nitrobenzylidene compound on treatment with amyl nitrite and hydrochloric acid affords β-isatoxime.

1-Amino-oxindole condensed with isatin in hot acetic acid to form N-*aminoisoindigotin*, yellow needles, m. p. 205—207°; this gave the indophenin reaction. 1-Acetamido-oxindole also condensed with isatin to form N-*acetamidoisoindigotin* (a bright red, microcrystalline powder, m. p. 303—306° [indef.]), which dissolved easily in dilute alkali, from which it was reprecipitated by acids. A solution of *N*-amino*iso*indigotin in aqueous potassium hydroxide on acidification gave a *substance*, $C_{16}H_{13}O_3N_3$, golden-yellow leaflets, m. p. 234—236°, which was insoluble in sodium carbonate but soluble in warm dilute alkali. On condensing 1-amino-oxindole with isatin in absolute alcohol in presence of piperidine a *substance* (annexed formula), was obtained as ivory-coloured leaflets, m. p. (decomp.) 208° upwards. On heating with alcoholic potassium hydroxide and acidifying, the yellow *isomeride*, $C_{16}H_{13}O_3N_3$, m. p. 234—236°, was obtained. N-*Aminoindirubin* was obtained by condensing 1-amino-oxindole and isatin-α-anil in alcoholic solution and formed almost black needles, m. p. (indef.) 253—256° (with previous sublimation). N-*Acetamidoindirubin* was obtained similarly from 1-acetamido-oxindole and isatin-α-anil as reddish-violet needles, m. p. about 299—302° (with previous sublimation). 1-*Acetamido-oxindole* forms colourless needles ($+1H_2O$), m. p. 186—187°. 1-*Benzoylamido-oxindole* forms faintly coloured leaflets, m. p. 189°. Both the acetyl and benzoyl com-

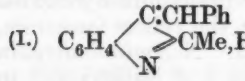
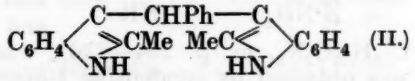


pounds are soluble in dilute alkalis. Treatment of 1-acetamido-oxindole in acetic acid with amyl nitrite and hydrochloric acid gave bright green needles of N-*acetamido*-β-*isatoxime* (annexed formula), m. p. 245—246° (decomp.); this, when boiled with sulphuric acid (1 : 3), afforded indazole-3-carboxylic acid. Condensation of 1-acetamido-oxindole with *p*-nitrosodimethylaniline gave N-*acetamidoisatin*-β-p-*dimethylamino-anil* as a dark brown powder, m. p. 214° (with previous sublimation) (red *sodium* salt, soluble), which with dilute mineral acids gave indazolecarboxylic acid. 1-Acetamido-oxindole was converted by dimethyl sulphate into 1-*acetylmethylamino-oxindole*, colourless leaflets, m. p. 146°; treatment with amyl nitrite and hydrochloric acid gave N-*acetylmethylamino*-β-*isatoxime*, greenish-yellow needles, m. p. 192—194° (*methyl ether*, yellowish-brown leaflets, m. p. 205—207°; also obtained directly by methylation of *N*-acetamido-β-isatoxime). On boiling the oxime with dilute sulphuric acid, 2-*methylindazole*-3-*carboxylic acid* was obtained as colourless leaflets, m. p. 215° (decomp.). Complete methylation of 1-amino-oxindole afforded 1-*dimethylamino-oxindole* as colourless leaflets, m. p. 81°; this condensed with nitrosobenzene in presence of piperidine to give N-*dimethylaminoisatin*-3-*anil*, orange needles, m. p. 125°, which when hydrolysed gave N-*dimethylaminoisatin*, dark red needles, m.p. 239°. 1-Dimethylamino-oxindole on treatment with amyl nitrite in hydrochloric–acetic acid solution afforded N-*dimethylamino*-β-*isatoxime*, yellow needles, m. p. 166—167°.



F. A. M.

The Humin formed by Acid Hydrolysis of Proteins. VIII. Condensation of Indole Derivatives with Aldehydes. G. O. Burr and R. A. Gortner (*J. Amer. Chem. Soc.*, 1924, **46**, 1224—1246; cf. Freund and Lebach, A., 1905, i, 663).—2-Methylindole condenses with benzaldehyde in presence of concentrated sulphuric acid to form *phenyl-2-methylindolidenemethane hydrogen sulphate* (I), orange needles, darkening above 100°, m. p. 172—173° with re-solidification at 175°. The free base was amorphous. On boiling with water, the sulphate is converted into phenyldi-2-methylindylmethane (II) (Fischer's " benzylidene dimethyl ketole ") and benzaldehyde, the reaction being reversed in presence of concentrated sulphuric acid.

(I.)  (II.) 

p-*Dimethylaminophenyl-2-methylindolidenemethane hydrochloride*, similarly obtained using hydrogen chloride as condensing agent, forms a hard, golden mass, m. p. 150—160°, purple-red in solution. The *base* has m. p. about 100°, dependent on the rate of heating. Its alcoholic solution is colourless at p_H 7·58, brilliant red at p_H 6·48. It yields a humin-like material on treatment with alcoholic hydrogen chloride, and both substances form ferrocyanides of the com-

position $(Base)_4,H_4Fe(CN)_6,2H_2O$. The violet humin-like base similarly obtained from *o*-hydroxyphenyl-2-methylindolidenemethane has m. p. 305°. *Anisyl-2-methylindolidenemethane hydrochloride*, golden, irregular plates, m. p. 181° (darkening at 155°); *cinnamyl-2-methylindolidenemethane hydrochloride*, golden needles, blackening at 160°, sintering at 180°, m. p. 195—205°; *o-tolyl-2-methylindolidenemethane hydrochloride*, yellow prisms, m. p. 178° (darkening at 165°); *p-hydroxyphenyl-2-methylindolidenemethane hydrochloride*, orange-red plates and wedges, m. p. 189°; *m-nitrophenyl-2-methylindolidenemethane*, a brown powder, exploding at a high temperature; and *2 : 4 : 6-trinitrophenyl-2-methylindolidenemethane*, minute, orange needles, m. p. 152°, are described. 2-Phenylindole condenses with benzaldehyde (excess) in presence of sulphuric acid, to form Fischer's " benzylidene-Pr_2-phenylindol." Using excess of sulphuric acid, *phenyl-2-phenylindolidenemethane* is formed as an orange powder, m. p. 182—184°, hydrolysed by boiling water to *benzylidenedi-2-phenylindole*. *p-Hydroxyphenyl-2-phenylindolidenemethane hydrochloride*, red prisms, m. p. indef.; *cinnamyl-2-phenylindolidenemethane*, a brown powder, m. p. 146—148°; *o-hydroxyphenyl-2-phenylindolidenemethane hydrochloride*, minute needles, sintering at 165°, but having no m. p.; *o-chlorophenyl-2-phenylindolidenemethane hydrochloride*, an orange powder, m. p. 212—214°; *anisyl-2-phenylindolidenemethane*, a red powder, m. p. indef.; *p-dimethylaminophenyl-2-phenylindolidenemethane*, a purple powder, m. p. 155°; *o-tolyl-2-phenylindolidenemethane*, a brownish-yellow powder; *m-nitrophenyl-2-phenylindolidenemethane*, a yellow powder; and *2 : 4 : 6-trinitrophenyl-2-phenylindolidenemethane*, an unstable, orange powder, are described. 2 : 3-Diphenylindole gave no condensation products analogous with the above, benzaldehyde etc. giving a grey, powdery *substance*, m. p. 123°. 2-Phenyl-3-methylindole yielded, similarly, a grey *substance*, m. p. 221—223°. Tryptophan condenses with salicylaldehyde with formation of a grey, powdery *substance*, $C_{12}H_{24}O_5N_2Cl$, excess of the aldehyde giving a humin. Humin-like products, derived from the condensation of 1 mol. of the indole with 2 mols. of aldehyde, were obtained by boiling the indoles, or the primary condensation products analogous to (I) and (II) above, with excess of the appropriate aldehyde in 20% hydrochloric acid. Yields were generally quantitative except with trinitrobenzaldehyde; humins were not obtainable from 2 : 3-diphenylindole. The solubilities of the humin hydrochlorides in acids, alkalis, and organic solvents, the solubility of the bases in ether, and their fusibility are tabulated. The artificial humins are precipitated from chloroacetic acid solution by water, but fibrin humins require the addition of hydrochloric acid to bring about coagulation. Humins of constant composition cannot be obtained from proteins. The humin from *o*-tolualdehyde and 2-methylindole was the most readily purified, whilst 2-phenylindole and benzaldehyde gave the only oxygen-free humin. The mol. weights of two fibrin humins, determined cryoscopically in chloroacetic acid, were found to be 439 and 760—780, respectively. Mol.-weight determinations of the indole humins in aniline were

unsuccessful. In phenol, the values obtained indicated that humin formation from 1 mol. of indole and 2 mols. of aldehyde is accompanied by polymerisation of the simple end-product. In benzene, further association was found in the one case examined. The mol. weights of hydrolytic humins and those derived from aromatic aldehydes were of the same order, whilst those derived from formaldehyde and indoles were much higher. 2-Methylindole remains unchanged on boiling with 20% hydrochloric acid. Phenyl-2-methylindolidenemethane hydrogen sulphate loses 1 mol. of water at 140—150°, with formation of a sulphonic acid. It yields amorphous, reddish-violet products on boiling with acids or on exposing its solutions to the light of a tungsten lamp. Some of these products condense more readily with benzaldehyde than does the original substance, indicating that humin formation from the indolidenemethane intermediates is preceded by molecular rearrangement. The humins obtained from 2-methylindole and benzaldehyde, 2 : 4 : 6-trinitrobenzaldehyde, and *o*-tolualdehyde, respectively, were stable to alkaline permanganate or alkali fusion, but were completely oxidised (to benzoic acid) by boiling chromic–acetic acid. The *o*-tolualdehyde humin formed a black, amorphous *dibromide*, $C_{25}H_{21}NBr_2$, the humin being regenerated by the action of sodium in alcohol. An unstable hydrochloride, but no picrate, was obtained. F. G. W.

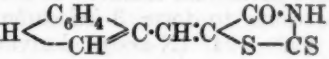
Isatin. Condensation of Isatin with Phenylhydroxylamine. H. Rupe and E. Stöcklin (*Helv. Chim. Acta*, 1924, **7**, 557—566).—Isatin reacts readily with phenylhydroxylamine to form *isatinphenylhydroxylamine*, $C_6H_4<^{CO}_{N}>C\cdot NPh\cdot OH$, large, red needles, m. p. 216° (decomp.), which is decomposed by alkalis into isatinic acid and phenylhydroxylamine. The same compound is obtained from isatin chloride and phenylhydroxylamine. With methyl sulphate in presence of alkali it gives O-*methylisatin*-β-*phenylhydroxylamine*, long, orange prisms, m. p. 152° (decomp.). On one occasion an *isomeride*, probably the *N*-methyl derivative, brown crystals, m. p. 181° (decomp.), was obtained, which, unlike the *O*-ether, is readily hydrolysed by alkali. The O-*acetyl* derivative of isatinphenylhydroxylamine, long needles, m. p. 179° (decomp.), and the O-*benzoyl* derivative, orange needles, m. p. 196°, are stable in presence of alkali. By the action of thionyl chloride on isatinphenylhydroxylamine, *isatin*-N-*chloroanilide*, $C_8H_4ON\cdot NPh\cdot Cl$, is obtained, small, brownish-red tablets, m. p. 182°. Isatinphenylhydroxylamine reacts with phenylhydrazine and semicarbazide to form isatinphenylhydrazone and isatinsemicarbazone. 7-*Methylisatin*-β-*phenylhydroxylamine* forms dark red crystals, m. p. 222—225° (decomp.).

By condensing 5-nitroisatin with phenylhydroxylamine, or by nitrating isatinphenylhydroxylamine with nitric acid (*d* 1·35), 5-*nitroisatinphenylhydroxylamine* is obtained, glistening bronze leaflets, m. p. 227° (decomp.). Its O-*methyl* ether forms orange, felted needles, m. p. 213°, and its *benzoyl* derivative, orange needles,

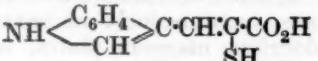
m. p. 203°. The nitro compound is readily soluble in alkalis, even in ammonia, with a deep red colour, and probably has the pseudo-acid structure, $NO_2H{\cdot}C_6H_3\langle{}^{CO}_{N}\rangle C{:}NPh{:}O$.

A new nitro derivative of isatin, 6-*nitroisatin*, obtained by nitrating isatin in concentrated sulphuric acid, forms reddish-yellow needles, m. p. 244°. 6-*Nitroisatin*-β-*phenylhydroxylamine* forms long needles, m. p. 224—227°, much redder than the 5-nitro derivative. E. H. R.

Use of Rhodanine in Organic Syntheses. IV. Indole- and Furyl-pyruvic Acids. C. Gränacher, M. Gerö, and V. Schelling (*Helv. Chim. Acta*, 1924, **7**, 575—578; cf. A., 1923, i, 706, 713).—3-Indolealdehyde condenses with rhodanine in acetic acid or acetic anhydride to form 3-*indolylidenerhodanine* (I), glistening brown leaflets, decomposing above 200°. This substance is converted by hot potassium hydroxide solution into α-*thiol*-β-3-*indoleacrylic acid* (II), an orange powder, decomp. 190°. When the



(I.)



(II.)

ammonium salt of this acid is warmed in solution with lead powder, it is converted into β-3-indolepyruvic acid, $C_8H_6N{\cdot}CH_2{\cdot}CO{\cdot}CO_2H$.

β-2-*Furylpyruvic acid* has been obtained by hydrolysing α-oximino-β-2-furylpyruvic acid (A., 1922, i, 850) with sulphurous acid. It forms unstable, pale yellow needles, m. p. 131°. E. H. R.

Use of Rhodanine in Organic Syntheses. V. Indole-2-carboxylic acid. C. Gränacher, A. Mahal, and M. Gerö (*Helv. Chim. Acta*, 1924, **7**, 579—586).—A new synthesis of indole-2-carboxylic acid is described. *o*-Nitrobenzylidenerhodanine (Bondzyński, A., 1887, 1108) is reduced in aqueous solution with ferrous hydroxide, and the solution of *o*-aminobenzylidenerhodanine, after making strongly alkaline with sodium hydroxide, is filtered and boiled, whereby α-thiol-*o*-aminocinnamic acid is formed. Ammonium chloride is added in small portions, whereupon a vigorous reaction ensues, and the resulting indole-2-carboxylic acid is precipitated by acidification. Ethyl indole-2-carboxylate (m. p. 124—125°) condenses with benzaldehyde to form *ethyl phenyl*-3 : 3′-*di-indylmethane*-2 : 2′-*dicarboxylate*, $CHPh(C_8H_5N{\cdot}CO_2Et)_2$, white needles, m. p. 239°; the corresponding *acid* crystallises in needles containing 1 mol. of alcohol, m. p. 243—244° (decomp.); *potassium* salt, $C_{25}H_{16}O_4N_2K_2,H_2O$. Similarly, *p*-anisaldehyde condenses to give *ethyl* p-*methoxyphenyl*-3 : 3′-*di-indylmethane*-2 : 2′-*dicarboxylate*, white crystals, m. p. 222° (decomp.); the corresponding *acid* has m. p. 267° (decomp.), and turns red on exposure to air. Formaldehyde condenses with ethyl indole-2-carboxylate to give, in poor yield, *ethyl* 3 : 3′-*di-indylmethane*-2 : 2′-*dicarboxylate*, a yellow, crystalline powder, m. p. 260° (decomp.); the *acid* forms pale yellow needles containing 1 mol of alcohol, m. p. 265°. E. H. R.

Formation of 3-Halogencarbazoles from Carbazole-3-diazonium Halides. S. H. TUCKER (*J. Chem. Soc.*, 1924, **125**, 1144—1148).—Carbazole-3-diazonium chloride has been obtained (cf. T., 1922, **122**, 2711) anhydrous and as di- and trihydrates. When treated, in acetone solution, with copper-bronze it yields a yellow product which, when acetylated, yields 3-chloro-*N*-acetylcarbazole, and this on hydrolysis gives 3-chlorocarbazole. *Carbazole-3-diazonium bromide*, $C_{12}H_8N_3Br,2H_2O$, yellow crystals, m. p. 110° (decomp.), was prepared from 3-aminocarbazole, and also from carbazole-3-diazonium chloride and potassium bromide; by treatment, in methyl ethyl ketone, with copper-bronze and acetylating and hydrolysing the resulting product there is formed 3-bromocarbazole. 3-Acetoxy-*N*-acetylcarbazole is obtained when carbazole-3-diazonium bromide is boiled with acetic anhydride and a little concentrated sulphuric acid.

Carbazole-3-diazonium iodide, $C_{12}H_8N_3I,H_2O$, is precipitated as a canary-yellow, crystalline substance on mixing aqueous solutions of carbazole-3-diazonium chloride and potassium iodide. It decomposes spontaneously in organic solvents to form 3-*iodocarbazole*, colourless, nacreous plates, m. p. 192—194° (*N-acetyl* derivative, needles, m. p. 145—147°). C. J. S.

Condensation of Acetaldehyde with Ammonia in Presence of Alumina. A. E. TSCHITSCHIBABIN, P. A. MOSCHKIN, and L. S. TJASCHELOWA (*J. pr. Chem.*, 1924, [ii], **107**, 132—137).—The product obtained by passing acetaldehyde and ammonia over alumina at 300° resembled closely that from acetylene and ammonia (this vol., i, 313). The crude condensate contained neutral compounds (20—25%), secondary bases, and tertiary bases (42½% of the raw condensate or about 60% of the theoretical yield). Further examination was confined to the last mixture; it was fractionally distilled and then separated into its components by fractional precipitation of their picrates (cf. *loc. cit.*). α-Picoline, γ-picoline, and 2-methyl-5-ethylpyridine ("aldehyde-collidine") were present in nearly equal amounts, together with smaller quantities of β-collidine and the two other bases already described (*loc. cit.*). There were no indications that pyridine was formed. W. A. S.

Products formed when Paraldehyde and Aldehyde-ammonia are heated together. A. E. TSCHITSCHIBABIN and M. P. OPARINA (*J. pr. Chem.*, 1924, [ii], **107**, 138—144).—For comparison with the results obtained in other experiments (cf. foregoing abstracts) this condensation (Dürkopf and Schlaugk, A., 1888, 1314, etc.) has been reinvestigated. A mixture of paraldehyde (3 mols.) and aldehyde-ammonia (1 mol.), heated in a sealed tube for 4 hours at 220°, gives an oily product, one-third of which is insoluble in acid. The remainder, separated into its components by fractional distillation and precipitation with picric acid, consists (above 80%) of 2-methyl-5-ethylpyridine; about 11% is α-picoline, whilst γ-picoline and β-collidine are also present in small amount. There is also a little of the collidine (the picrate is now stated to have m. p. 139° and the chloroplatinate m. p. 190°) found in the

product of interaction of acetaldehyde and ammonia in presence of alumina. The trimethylpyridine of Knudsen and others (A., 1895, i, 562) and lutidine were not detected. W. A. S.

Condensation of Propionaldehyde with Ammonia. A. E. TSCHITSCHIBABIN and M. P. OPARINA (*J. pr. Chem.*, 1924, [ii], **107**, 145—154).—By passing propionaldehyde and ammonia over alumina at 310—320°, a product was obtained which consisted of neutral substances (about 50%), secondary bases (about 15%), and tertiary bases, the yield of which therefore was about 40% of the theoretical, in agreement with that obtained by other methods (cf. Dürkopf and others, A., 1890, 1002, etc.). The mixture of tertiary bases contained some tarry material of high b. p., but otherwise consisted almost entirely of the following three compounds: 3 : 5-dimethyl-2-ethylpyridine (picrate, yellow leaflets, m. p. 156—157°, cf. Dürkopf, *loc. cit.*), about 60%; 3 : 5-*dimethyl*-4-*ethylpyridine* (b. p. 219—220°/748 mm., $d_4^{26\cdot7}$ 0·9516, $n_D^{26\cdot7}$ 1·5064; *picrate*, prisms, m. p. 155—156°), about 23%; this substance was isolated by Dürkopf (*loc. cit.*), who supposed it to be a tetramethylpyridine; the authors have now oxidised it to 4-*ethylpyridine*-3 : 5-*dicarboxylic acid*, m. p. 261° (decomp.), and converted the latter into 4-ethylpyridine (cf. Tschitschibabin, A., 1906, i, 451). The remaining 17—18% of the mixture is 3 : 5-dimethylpyridine. W. A. S.

Synthesis of Pyridine from Aldehydes and Ammonia. A. E. TSCHITSCHIBABIN and M. P. OPARINA (*J. pr. Chem.*, 1924, [ii], **107**, 154—158).—A more detailed account of work already noted (this vol., i, 312). W. A. S.

2-Amino-4-methylpyridine and certain Derivatives. O. SEIDE (*Ber.*, 1924, **57**, [*B*], 791—794; cf. Tschitschibabin and Zeide, A., 1915, i, 590; Zeide, A., 1923, i, 600).—2-*Amino*-4-*methylpyridine*, lustrous leaflets, m. p. 98°, is prepared by the action of sodamide on 4-methylpyridine dissolved in boiling xylene; the *hydrochloride*, m. p. 176—177°, *nitrate*, m. p. 139°, *picrate*, m. p. 227° (decomp.), and *chloroplatinate*, m. p. 208°, are described. 2-*Acetylamino*-4-*methylpyridine*, colourless prisms, m. p. 102—103°, yields a *picrate*, yellow needles. Benzoylation of 2-amino-4-methylpyridine gives a mixture of the *dibenzoyl* derivative, colourless needles, m. p. 182—183°, and *monobenzoyl* compound, colourless prisms, m. p. 114°. Diazotisation of 2-amino-4-methylpyridine in very concentrated hydrochloric acid solution yields mainly 2-*chloro*-4-*methylpyridine*, a colourless liquid, b. p. 194—195°, d_4^{20} 1·1459, n_D^s 1·5293 [*chloroplatinate*, orange-coloured prisms ($+H_2O$) which blacken at 219° but do not melt below 290°]; 2-*hydroxy*-4-*methylpyridine*, rhombs, m. p. 130° (*monohydrate*, m. p. 65°), is produced in minor amount, but is more conveniently prepared by diazotisation of the amine dissolved in dilute hydrochloric acid. 4-Amino-2-methylpyridine dissolved in concentrated sulphuric acid is converted by nitric acid (*d* 1·4) at 0° into 2-*nitroamino*-4-*methylpyridine*, pale yellow prisms, m. p. 182° (decomp.), which is transformed by prolonged contact with sulphuric acid at the

atmospheric temperature into a mixture of (?) 3-*nitro*-2-*amino*-4-*methylpyridine*, yellow needles, m. p. 136°, and (?) 5-*nitro*-2-*amino*-4-*methylpyridine*, yellow prisms, m. p. 220°. H. W.

Constitution of Roth's 2-Stilbazolealkine and Synthesis of 2-Stilbazole*iso*alkine. C. Räth (*Ber.*, 1924, **57**, [*B*], 840—842).—Pyridine-2-aldehyde (cf. Lénart, A., 1914, i, 574) is converted by magnesium benzyl bromide into 2-α-*hydroxy*-β-*phenylethylpyridine*, colourless cubes, m. p. 104° (the *hydrochloride*, leaflets, m. p. 152°, and the non-crystalline *picrate* are described). It is not identical with the compound described by Roth (A., 1901, i, 165), which must therefore be 2-β-hydroxy-β-phenylethylpyridine. H. W.

Dihydroquinoline Bases. G. Heller (*Ber.*, 1924, **57**, [*B*], 764; cf. Räth, this vol., i, 555).—The compound considered by Doebner (A., 1898, i, 384) to be 2-methyldihydroquinoline should be deleted from the literature (cf. Heller and Sourlis, A., 1908, i, 914; Heller, A., 1911, i, 747). H. W.

Quinoline Dyestuffs. E. Rosenhauer [with A. Schmidt and W. Schleifenbaum] (*J. pr. Chem.*, 1924, [ii], **107**, 232—240).—2-Methylene-1-methyl-1:2-dihydroquinoline ("quinaldine*iso*-base") combines with bromine to form a perbromide-like compound, $C_{11}H_{11}NBr_3$ (yellow crystals, decomp. 152°), which decomposes when dissolved in acetone, giving bromoacetone and 2-*bromomethylquinoline methobromide*, pale yellow prisms, decomp. 205°. Either substance interacts with phenylhydrazine, giving 2-*benzeneazomethylene*-1-*methyldihydroquinoline hydrobromide*, violet needles, decomp. 250°; the corresponding *base* forms bronzy, dark red needles, m. p. 140—141°. Similar compounds were obtained with *p*-bromophenylhydrazine (*base*: red needles, m. p. [indef.] 162°; *hydrobromide*: needles, decomp. 259°) and *p*-nitrophenylhydrazine (*base*: bluish-green needles, decomp. 186°; *hydrobromide*: red needles, decomp. 248°). α-Bromomethylquinoline methobromide and *p*-aminodimethylaniline interact to give the *methobromide* (green prisms, decomp. 198°) corresponding with α-*p*-dimethylaminophenyliminomethylenequinoline ethiodide (Kaufmann and Valette, A., 1912, i, 655). The extension of these experiments to lepidine and α-picoline is announced. W. A. S.

1:1'-Dialkyltetrahydrodipyridyls. O. Mumm, O. Roder, and H. Ludwig (*Ber.*, 1924, **57**, [*B*], 865—880).—In continuation of previous work (Mumm and Beth, A., 1921, i, 686), the preparation is described of a 4:4'-disubstituted dipyridyl; it is bimolecular in freshly-prepared solution in freezing benzene, but gradually dissociates when preserved. It is intensely active chemically. Since, however, solutions which contain the unimolecular form are not intensely coloured, this activity is not ascribed to fission into radicals, but to the powerful "divided" partial valencies of the nitrogen and 2-carbon atoms.

Ethyl 1 : 2 : 4 : 6 : 1′ : 2′ : 4′ : 6′-*octamethyltetrahydro*-4 : 4′-*dipyridyl*-3 : 5 : 3′ : 5′-*tetracarboxylate*,

$$MeN<\begin{matrix}CMe{:}C(CO_2Et)\\CMe{:}C(CO_2Et)\end{matrix}>CMe\cdot MeC<\begin{matrix}C(CO_2Et){:}CMe\\C(CO_2Et){:}CMe\end{matrix}>NMe,$$

pale yellow, lustrous needles, m. p. 80—82°, is prepared in 90—100% yield by the action of sodium amalgam on an aqueous solution of ethyl 2 : 4 : 6-trimethylpyridine-3 : 5-dicarboxylate methosulphate (cf. Mumm and Hingst, this vol., i, 83) in an atmosphere of carbon dioxide. When heated above its m. p. in an atmosphere of hydrogen, it is transformed into equivalent amounts of ethyl 1 : 2 : 4 : 6-tetramethyldihydropyridine-3 : 5-dicarboxylate and ethyl trimethylmethylenedihydropyridine-3 : 5-dicarboxylate, m. p. 72—73° (cf. Mumm and Hingst, *loc. cit.*); a similar "disproportionation" is observed under the influence of dilute hydrochloric acid. The dipyridyl compound (1 mol.) reacts with iodine (2 atoms) in alcoholic solution in the absence of air to give ethyl 2 : 4 : 6-trimethylpyridine-3 : 5-dicarboxylate methiodide. As intermediate or by-products, the *periodides*, $C_{14}H_{19}O_4N,MeI,I_2$, m. p. 102—103°, and $C_{14}H_{19}O_4N,MeI,I$, m. p. 114°, are observed. These substances can also be prepared from ethyl 2 : 4 : 6-trimethylpyridine-3 : 5-dicarboxylate and iodine in alcoholic solution; they are bimolecular. The dipyridyl compound when dissolved in benzene absorbs oxygen very rapidly, giving ethyl trimethylmethylenedihydropyridine-3 : 5-dicarboxylate, mixed with small amounts of ethyl 1 : 2 : 4 : 6-tetramethyldihydropyridine-3 : 5-dicarboxylate. It is readily hydrogenated in alcoholic solution in the presence of colloidal palladium to the unsymmetrical ethyl 1 : 2 : 4 : 6-tetramethyldihydropyridine-3 : 5-dicarboxylate, b. p. 145—152°/0·3 mm. (cf. Mumm and Hingst, *loc. cit.*). The latter compound is most sharply differentiated from its isomeride, m. p. 85°, by its behaviour towards hydrogen in the presence of spongy platinum and glacial acetic acid, whereby it is converted solely into ethyl 1 : 2 : 4 : 6-tetramethyltetrahydropyridine-3 : 5-dicarboxylate (*picrate*, yellow rhombohedra, m. p. 130—131°); the solid isomeride is more slowly hydrogenated, but is ultimately transformed into *ethyl* 1 : 2 : 4 : 6-*tetramethylhexahydropyridine*-3 : 5-*dicarboxylate*, a pale yellow liquid, b. p. 162—164°/11 mm. (*picrate*, m. p. 153°; *hydrochloride*, m. p. 66°; *hydrobromide*, m. p. 48°; *additive* compound with mercuric chloride, m. p. 147°). The tetrahydro ester is more conveniently prepared by the catalytic hydrogenation of ethyl 2 : 4 : 6-trimethylpyridine-3 : 5-dicarboxylate methosulphate, whereby the hexahydro derivative is also produced in small amount (cf. Neuhaus, *Diss.* Kiel, 1923). H. W.

isoIndigotin. C. W. Hansen (*Ann. Chim.*, 1924, [x], **1**, 94—134). —*iso*Indogenides, formed by condensation of *o*- and *p*-chloroaldehydes and an *o*-sulphonated aldehyde with oxindole, were prepared (cf. Wahl and Bagard, A., 1909, i, 735; Stollé, A., 1914, i, 992; Martinet and Dornier, A., 1921, i, 516). The chloro derivatives have been described independently by Neber and Röcker (A., 1923, i, 945); *sodium benzylideneoxindole*-2-*sulphonate* forms pale yellow crystals.

*iso*Indogenides exhibit slight tinctorial properties. The leuco-compound obtained by reduction of indine (Wahl and Hansen, A., 1923, i, 607) yields from concentrated alkaline solution a *tetrabenzoyl* derivative, m. p. 209°, which indicates that under the conditions specified the leuco-compound exists wholly or in part as $C_6H_4<^{C}_{NH}>C\cdot OH\ OH\cdot C<^{C}_{NH}>C_6H_4$. Reduction of indine by means of zinc and acetic acid in presence of sodium acetate affords *diacetyl-leucoisoindigotin*, colourless crystals, m. p. 220°, isomeric with the diacetyl-leucoindigo described by Liebermann (A., 1888, 492). Disulphoisatide may be converted directly into indine by the action of ammonia in its alcoholic solution.

The paper contains a more detailed account of work already published on disulphoisatide, isatin, etc. (Wahl and Hansen, this vol., i, 322; cf. Dornier and Martinet, A., 1923, i, 852).

H. J. E.

Constitution of Salipyrine. S. Bodforss and A. Guthe (*Ber.*, 1924, **57**, [*B*], 842—846).—Although salipyrine is usually represented as antipyrine salicylate, it may possibly be an additive compound, *e.g.*, $CO_2H\cdot C_6H_4\cdot O...H...C_{11}H_{12}ON_2$. Antipyrine is a very weak base ($k=2\cdot8\times10^{-13}$), its salts in dilute solution being considerably hydrolysed. Aqueous or alcoholic solutions of salipyrine show only the reactions of its components. The alteration of *E.M.F.* produced by the addition of salipyrine to a cell containing a suspension of silver salicylate in saturated salicylic acid against a standard calomel electrode has been determined in comparison with the effect produced by the addition of acids and bases, and from the results it is concluded that undissociated salipyrine consists of an additive complex corresponding with the above formula. The conductivity of solutions of antipyrine hydrochloride has been studied and additive compounds of antipyrine with the following phenols have been obtained: vanillin, *p*-cresol, nitroresorcinol, protocatechualdehyde, and *p*-hydroxybenzaldehyde. R. B.

Thallous Picrolonate. M. Giua (*Gazzetta*, 1924, **54**, 204—206).—Almost pure thallous carbonate is obtainable in good yield by passing dried air through 95% or absolute ethyl, propyl, *iso*butyl, or *iso*amyl alcohol containing in suspension thallium in powder or thin strips.

Thallous picrolonate, $C_{10}H_7O_5N_4Tl$, separates when a dilute acetic acid solution of picrolonic acid is added to a similar solution of the carbonate, and forms pale yellow needles, exploding above 300°.

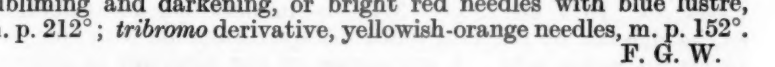
T. H. P.

Quinazolines. XXXV. Stereoisomeric Styryl Derivatives of some 4-Quinazolone Alkiodides, and their Bearing upon the Problem of Photosensitising Dyes. M. T. Bogert and H. Clark (*J. Amer. Chem. Soc.*, 1924, **46**, 1294—1301).—Quaternary alkyl salts could not be obtained from 2 : 4-dimethyl-, 2-styryl-4-methyl-, and 2-phenyl-4-methyl-quinazolines; 2 : 4-dimethylquinazoline could not be condensed with aromatic aldehydes. The

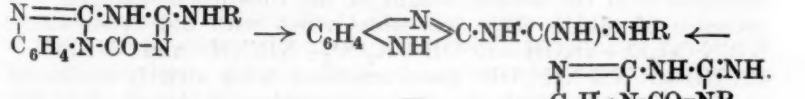
condensation of substituted 4-quinazolone alkiodides with *p*-dimethylaminobenzaldehyde yielded 2-*p*-dimethylaminostyryl-4-quinazolone alkiodides, the stereoisomeride obtained being dependent on whether piperidine or acetic anhydride was used as condensing agent, or, using the latter, on the conditions of experiment. The stable (purple) isomerides had higher m. p. than the (red) labile isomerides. The latter were converted into the stable forms by acetic anhydride at 120°, but the reverse change could not be effected. Both isomerides yielded the same monobromo-dibromides. The products have no value as dyes or photosensitisers. The following compounds are described. 2-p-*Dimethylaminostyryl-4-quinazolone methiodide*, reddish-purple needles, m. p. 265·7° (decomp.) with previous sublimation or darkening, or bright red needles, m. p. 214°; 2-p-*dimethylaminostyryl-3-methyl-4-quinazolone methiodide*, similar, m. p. 263·5° (decomp.) after subliming and darkening, or m. p. 216° (decomp.); *tribromo* derivative, orange needles, m. p. 178°; 2-p-*dimethylaminostyryl-3-methyl-4-quinazolone ethiodide*, similar, m. p. 264·7° (decomp.) after subliming and darkening, or m. p. 205·5°; 2-p-*dimethylaminostyryl-3-ethyl-4-quinazolone methiodide*, similar, m. p. 255° (decomp.) after subliming and darkening, or bright red needles with blue lustre, m. p. 212°; *tribromo* derivative, yellowish-orange needles, m. p. 152°.

F. G. W.

Action of Cyanogen Halides on Phenylhydrazine. VIII. Exo-alkyl Derivatives of Melamine. G. Pellizzari (*Gazzetta*, 1924, **54**, 177—184).—*o*-Phenyleneammelyl chloride (cf. A., 1922, i, 585) reacts readily with primary amines to form melaminic bases having the alkyl group united to a nitrogen atom which does not form part of the nucleus:

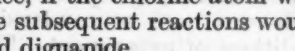


Such *exo*-alkylphenylenemelamines are isomeric with those obtained from the same amines and dicyanophenyleneguanidine (A., 1921, i, 620). Phenyleneammelyl chloride reacts also with secondary amines; with methylaniline, *e.g.*, it gives phenyl-*exo*-phenylenemethylmelamine (a white, crystalline powder, not melting at 300°), which is formed also by direct addition of methylaniline to dicyanophenyleneguanidine. Phenyleneammelyl chloride acts also on ammonia, giving a compound identical with that formed by direct addition of ammonia to phenyleneguanidine. When heated with hydrochloric acid, the *exo*-alkylphenylenemelamines behave like their isomerides, giving the corresponding ammelines. Treatment of the *exo*-ammelines thus formed with hot potassium hydroxide solution affords a single substituted diguanide, even from a pair of isomeric compounds:

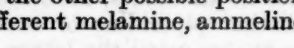


This result confirms the scheme given for the addition of hydrogen chloride to αβ-dicyano-*o*-phenyleneguanidine (A., 1922, i, 585), since, if the chlorine atom were fixed in the other possible position, the subsequent reactions would yield different melamine, ammeline, and diguanide.

Phenyl-exo-*phenylenemelamine* (I) is basic and forms minute needles not melting at 300°.



(I.)



(II.)

Phenyl-exo-*phenyleneammeline* (II), forms a white powder with high m. p. (decomp.).

Phenyl-exo-*phenylenemethylammeline*, $C_{16}H_{13}ON_5$, forms a white, microcrystalline powder, exhibits both acid and basic properties, and forms a *hydrochloride* ($+H_2O$). *o-Phenyleneguanylphenylmethylguanidine*, $C_6H_4<^{N}_{NH}>C\cdot NH\cdot C(NH)\cdot NMePh$, forms colourless, lustrous, flat needles, m. p. 163°. T. H. P.

Thiazoles. IV. The Synthesis of Benzthiazoles from o-Nitrochlorobenzene. M. T. Bogert and F. D. Snell (*J. Amer. Chem. Soc.*, 1924, **46**, 1308—1311).—*o*-Aminothiophenol is obtained as the zinc salt by reducing *o*-nitrophenyl disulphide with zinc dust in glacial acetic acid. A suspension of the zinc salt in aqueous ammonium hydroxide is oxidised by a current of air to *o*-aminophenyl disulphide. 2-Phenylbenzthiazole is obtained by boiling the zinc salt of *o*-aminothiophenol with benzoyl chloride, or *o*-benzoylaminophenyl disulphide (m. p. 142·6°) with tin and dilute hydrochloric acid (etc.). 2-p-*Nitrophenylbenzthiazole*, similarly obtained, forms nearly colourless needles, m. p. 231°, and when reduced gives the corresponding amino derivative, which is also obtained by the reduction of 2-p-*nitrobenzoylaminophenyl disulphide*, pale yellow prisms, m. p. 217° (decomp.). F. G. W.

Azoxy-esters. A. Pieroni and G. Giannini (*Gazzetta*, 1924, **54**, 162—177).—The authors have prepared various members of a new class of compounds of the formula $R\cdot N_2O\cdot CO_2Et$, in which R represents an aromatic residue, by treating the corresponding azo-esters with peracetic acid for a period of some months (cf. Angeli, A., 1917, i, 228, 417).

By treating ethyl chlorocarbonate with the phenylhydrazine in pyridine solution (cf. Busch and Heinrichs, A., 1900, i, 314) almost quantitative yields may be obtained of ethyl phenylhydrazinecarboxylate (cf. Widman, A., 1895, i, 603) and of its *p*-chloro- and *p*-bromo-derivatives. Oxidation of these hydrazine compounds by means of potassium permanganate in acetic acid solution yields the corresponding azo-esters as deep red liquids of high density, which increases with the atomic weight of the substituent halogen. In presence of alkali, these azo-esters react with aldehydes thus: $NR{:}N\cdot CO_2Et+2KOH=Et\cdot OH+K_2CO_3+NR{:}NH$ and $NR{:}NH+R\cdot CHO=R\cdot NH\cdot NH\cdot COR$, these reactions being strictly analogous to those occurring with the azocarbonamides (cf. Angeli, A. 1917,

i, 228) and with the azoxy-esters (*vide infra*), from which normal diazotates are thus formed.

Treatment of the azo-esters in alcoholic solution with alcoholic potassium hydroxide results in the immediate separation of the potassium salts of the azocarboxylic acids, previously obtained from the azocarbonamides only by more or less complicated treatment (cf. Widman, *loc. cit.*; Thiele, A., 1896, i, 94). The corresponding silver and lead salts, prepared from the potassium salts by double decomposition, immediately decompose with copious liberation of nitrogen.

The azoxy-esters are dense, pale yellow, oily liquids, which in the light become brown, probably owing to the occurrence of a transformation similar to that taking place with azoxybenzene, $O{:}NPh{\cdot}NPh \longrightarrow OH{\cdot}C_6H_4{\cdot}N{:}NPh$. Since the azoxy-esters are indifferent to the halogens, the constitution $O{:}NR{:}N{\cdot}CO_2Et$ must be attributed to them. Just as was found with phenylazocarbonamide, the other isomeride is not formed under the conditions of oxidation employed, probably owing to the influence of the negative carbonyl group attached to the nitrogen atom.

When treated with alkali, the azoxy-esters undergo decomposition analogous to that shown by the azo derivatives, giving a normal diazotate, $O{:}NR{:}NH$ (cf. Angeli, *loc. cit.*), which is unstable and decomposes, with formation of ammonia and a nitro derivative: $O{:}NPh{:}NH + H_2O = NH_3 + Ph{\cdot}NO_2$.

When the oxidation of the azo-esters by peracetic acid is carried out at 50—60°, the azoxy-esters formed are accompanied by (1) the corresponding azoxybenzenes, which are probably due to the reaction $O{:}NR{:}N{\cdot}CO_2Et + NR{:}N{\cdot}CO_2Et \longrightarrow O{:}NR{:}NR$, but may result from the oxidation of the azobenzenes formed as intermediate products; (2) chloro- or bromo-benzoic acid, the origin of which is as yet uncertain.

By a procedure analogous to that followed for the preparation of the hydrazo-esters, attempts have been made to obtain from the acid $CO_2H{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2$ the hydrazo-ester, $CO_2H{\cdot}C_6H_4{\cdot}NH{\cdot}NH{\cdot}CO_2Et$, but the resulting compound contains a mol. of water less than the latter and is regarded as ethyl *o*-hydrazinobenzoylcarboxylate, $C_6H_4{<}\overset{CO}{NH}{>}N{\cdot}CO_2Et$. *Ethyl phenylhydrazinocarboxylate*,

$$NHPh{\cdot}NH{\cdot}CO_2Et,$$

forms white crystals, m. p. 85°; *ethyl* p-*chlorophenylhydrazinocarboxylate*, white needles, m. p. 92—93°, and *ethyl* p-*bromophenylhydrazinocarboxylate*, white needles, m. p. 110—111°; all these esters colour slightly in the air and light.

Ethyl benzeneazocarboxylate, $NPh{:}N{\cdot}CO_2Et$, gives the iodoform reaction in methyl-alcoholic solution. *Ethyl* p-*chloro-* and p-*bromobenzeneazocarboxylates* show the same reaction. The three corresponding *potassium* salts form golden-yellow leaflets. *Ethyl benzeneazoxycarboxylate*, $O{:}NPh{:}N{\cdot}CO_2Et$, was obtained as a slightly impure, straw-yellow oil and gives the iodoform reaction in methyl-alcoholic solution. *Ethyl* p-*chloro-* and p-*bromo-benzeneazoxycarboxylates* were not obtained sufficiently pure for analysis.

Ethyl o-*hydrazinobenzoylcarboxylate* has m. p. 194°. The *silver* derivative, $C_6H_4<\begin{matrix}CO\\NAg\end{matrix}>N\cdot CO_2Et$, and the corresponding *mercurous* compound form colloidal solutions and gradually decompose when separated as hydrogels. The *mercurichloride*,

$$C_6H_4<\begin{matrix}CO\\N(\cdot HgCl)\end{matrix}>N\cdot CO_2Et,$$

forms a microcrystalline, white precipitate. *Potassium* o-*hydrazinobenzoylcarboxylate*, which was not obtained pure, instantly reduces ammoniacal silver nitrate solution. T. H. P.

Azoxyamides and Pyrroles. A. Pieroni (*Gazzetta*, 1924, **54**, 157—161).—Like phenyldiazonium chloride (cf. Fischer and Hepp, A., 1886, 1041; Plancher and Soncini, A., 1903, i, 449), azoxyamides react with pyrrole and a number of its derivatives, yielding azo compounds. This reaction is effected best by *p*-bromo- and *p*-chloro-phenylazoxycarbonamides, which in an alkaline medium react in the usual way:

$$O{:}NR{:}N\cdot CO\cdot NH_2 \longrightarrow O{:}NR{:}N\cdot CO_2H \longrightarrow O{:}NR{:}NH,$$

coupling with the pyrrole then following. A similar reaction takes place between phenylazoxycarbonamides and indole, the azo group entering in the 3-position of the pyrrole nucleus.

2 : 2′-*Bis*-p-*bromobenzeneazopyrrole*, $C_{16}H_{11}N_5Br_2$, forms deep red crystals with copper reflection, m. p. 208°. p-*Bromobenzeneazoacetylpyrrole*, $C_{12}H_{10}ON_3Br$, crystallises in yellow laminæ, m. p. 168°. 2 : 5-*Dimethyl*-3-*benzeneazopyrrole* forms an orange-yellow, crystalline powder, m. p. 134°; 2 : 4-*dimethyl*-3-p-*bromobenzeneazopyrrole* has m. p. 152°. 3-p-*Bromobenzeneazoindole* crystallises in golden-yellow scales, m. p. 170°, and 3-*benzeneazoindole* in yellow crystals, m. p. 135°.

3-*Benzeneazoindole*-2-*carboxylic acid*, $C_{15}H_{11}O_2N_3$, obtained from sodium indole-2-carboxylate and benzeneazocarbonamide in methyl-alcoholic solution containing potassium methoxide, forms deep red, lustrous needles, m. p. 216° (decomp.). Its yellow solution in dilute alkali gives a precipitate of the red form on addition of mineral acid; its acetic acid solution is also red; it is therefore probably capable of the transposition:

$$C_6H_4<\begin{matrix}C(N_2Ph)\\NH\end{matrix}>C\cdot CO_2H \rightleftharpoons C_6H_4<\begin{matrix}C(:N\cdot NHPh)\\N\end{matrix}>C\cdot CO_2H.$$

The product obtained under similar conditions from indole-3-carboxylic acid loses carbon dioxide, forming 3-benzeneazoindole (*vide supra*); if, with the same acid, *p*-bromophenylazoxycarbonamide is used, 3-*p*-bromobenzeneazoindole, m. p. 170°, is obtained.

2-*Methyl*-3-p-*chlorobenzeneazoindole*, $C_{15}H_{12}N_3Cl$, forms yellow needles, m. p. 168°. T. H. P.

Reduction of Nitronaphthalenes. II. β-Nitronaphthalene. W. M. Cumming and G. S. Ferrier (*J. Chem. Soc.*, 1924, **125**, 1108—1111; cf. T., 1923, **123**, 2466).—The reduction of 2-nitronaphthalene with zinc dust and alcoholic ammonium chloride yields 2 : 2′-azoxynaphthalene, m. p. 164° (cf. Meisenheimer and Witte, A., 1904, i, 193), and 2 : 2′-azonaphthalene. Further reduction

undoubtedly occurs, giving hydrazonaphthalene; this at once undergoes atmospheric oxidation to 2 : 2′-azonaphthalene, or in absence of air, benzidine transformation to 2 : 2′-diamino-1 : 1′-dinaphthyl. 2 : 2′-Azonaphthalene is stable in air, but on oxidation with perhydrol in acetic acid yields 2 : 2′-azoxynaphthalene. Exposure to light in alcoholic solution converts 2 : 2′-azoxynaphthalene into a red *isomeride*, m. p. 162°, which, from a comparison of its absorption spectrum with that of 2-naphthaleneazo-2-naphthol, is considered to be a hydroxyazo compound (cf. Baudisch and Fürst, A., 1913, ii, 39). R. B.

Metallic Compounds of Dibenzoylhydrazide. A. Benrath (*J. pr. Chem.*, 1924, [ii], **107**, 211—224; cf. A., 1904, i, 935).—The solubility of dibenzoylhydrazide in water is 4·7 mg. per 100 c.c. at 17°. That of the monosodium derivative is 0·346 g./100 c.c. This salt is hydrolysed to the extent of 14% in aqueous solution and dibenzoylhydrazide is precipitated. The hydrolysis, therefore, is independent of the dilution; addition of sodium hydroxide lessens the hydrolysis but also decreases the solubility. Neutral salts, *e.g.*, sodium chloride, nitrate, or sulphate, likewise depress the solubility. The same behaviour is shown by the potassium salt; its solubility is 0·447 g./100 c.c. and it is hydrolysed 13·1%. The *lithium* salt, yellow crystals, has solubility 0·08 g./100 c.c. and 15·4% is hydrolysed. The *rubidium*, *cæsium*, *magnesium*, *calcium*, *barium*, *silver*, *thallium*, *copper*, *cobalt*, *nickel*, *zinc*, *cadmium*, and *manganese* salts are described, all being obtained by precipitation or double decomposition in an appropriate solvent. A third *lead* compound, $C_{14}H_{10}O_2N_2Pb$, a yellow powder, and two *mercury* derivatives, $[C_{14}H_{10}O_2N_2]_2Hg$ and $C_{14}H_{10}O_2N_2Hg,HgCl_2$, are also described. Dibenzoylhydrazide combines with metallic sodium in boiling toluene solution to a *disodium* compound, presumably CPh(ONa):N·N:CPh(ONa), a yellow substance. W. A. S.

Mechanism of the Decomposition of β-Bromophosphinic Acids in Alkaline Solution. J. B. Conant and E. L. Jackson (*J. Amer. Chem. Soc.*, 1924, **46**, 1003—1018; cf. A., 1923, i, 69).—Certain β-bromophosphinic acids of the type (I) are quantitatively decomposed in aqueous alkaline solution. It was thought that an inner ester analogous to a β-lactone (a β-"phostone") (II) might be formed as an intermediate product:

$$\begin{matrix} \text{CHR·CHBr·COR} \\ | \\ \text{A·POOH} \quad \text{(I.)} \end{matrix} \rightarrow \begin{matrix} \text{CHR·CH·COR} \\ | \quad | \\ \text{A·PO—O} \quad \text{(II.)} \end{matrix} \quad \begin{matrix} \text{(R=Aryl; A=·OH,} \\ \text{Ph· or PHO·).} \end{matrix}$$

Attempts to prepare such β-phostones were unsuccessful. β-p-*Chlorobenzoyl-α-phenylethylphosphinic acid*, colourless crystals with 1 mol. of water, m. p. 112—114°, was prepared by the action of phosphorus trichloride on *p*-chlorophenyl styryl ketone in glacial acetic acid. The β-*bromo* derivative, m. p. 204°, obtained by bromination in chloroform solution, was difficult to obtain pure. The *phenyl* ester, $C_6H_4Cl·CO·CH_2·CHPh·PO(OPh)_2$, obtained by the action of phenol and thionyl chloride on the acid, formed crystals, m. p. 109°. Partial hydrolysis of the latter yielded the *phenyl*

hydrogen ester, crystals, m. p. 180°. The β-*bromo* derivative of the phenyl ester had m. p. 127—129°. The β-*bromo* derivative of the phenyl hydrogen ester forms two *isomerides*, one, difficultly soluble in 5% sodium hydrogen carbonate, m. p. 195—196°, the other readily soluble, m. p. 150—151°. Both isomerides were decomposed by cold dilute sodium hydroxide with formation of *p*-chlorophenyl styryl ketone, showing them to be stereoisomerides. They were soluble in aqueous sodium carbonate without decomposition. It was not found possible by warming to eliminate the bromine atom (with β-phostone formation) without also splitting off the phosphinic group. Experiments carried out in "buffer" solutions of various alkalinities showed that the rate of decomposition was a function of the hydroxyl-ion concentration. This together with other evidence excludes β-phostone formation as an intermediate step in the decomposition of β-bromophosphinic acids. To obtain the corresponding methyl esters as crystallisable products with satisfactory yields, it was necessary to use a Carius tube. *Methyl hydrogen* β-p-*chlorobenzoyl-α-phenylethylphosphinate*, m. p. 152—153°, is obtained in 65—74% of the theoretical yield. It is accompanied by *methyl* β-p-*chlorobenzoyl-α-phenylethylphosphinate*, m. p. 123—124°. They are separated by means of sodium carbonate solution, in which only the former is soluble. The β-*bromo* derivative of the monomethyl ester is difficult to obtain pure (yield 25% of theory, m. p. 163—164°). It dissolves readily in sodium hydroxide with loss of the bromine atom. Its rate of decomposition was studied. The chief decomposition product was a monomethyl ester of either an unsaturated or a hydroxy-phosphinic acid. It is suggested that the first step in the decomposition of the β-bromophosphinic acids is the interaction of the organic molecule and the hydroxyl ion to form an unstable ionised hydroxyl compound. The further decomposition may take place in various ways corresponding with the several products obtained by the action of alkalis on different types of bromophosphinic acids. A. C.

Complex Boric Acid Compounds and the Optically Active Boron Atom. J. Böeseken and J. Meulenhoff (*Proc. K. Akad. Wetensch.*, 1924, 27, 174—177).—The ammonium, aniline, *p*-chloroaniline, dimethylaniline, and pyridine salts of the dipyrocatechol–boric acid compound (cf. A., 1923, i, 557; ii, 406) have the composition $[B(O_2C_6H_4)_2]M$ or $[B(O_2C_6H_4)_2]H,NH_2R$, and form anhydrous crystals; the ammonium salt appears to volatilise unchanged. The free acid has the composition $[B(O_2C_6H_4)_2]H$. The aniline and pyridine salts of the dipyrogallol–boric acid compound have also been prepared, and likewise the potassium, ammonium, and aniline salts of the di-(3-nitropyrocatechol) and the di-(4-nitropyrocatechol) compounds, these having the constitution $[B(O_2C_6H_3{\cdot}NO_2)_2]R$ and forming anhydrous crystals.

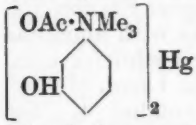
The salicylic acid–boric acid compound forms anhydrous aniline, ammonium, potassium, sodium, and silver salts, $[B(O_2COC_6H_4)_2]R$, whilst the pyridine salt contains 1 mol., and the zinc, copper, cobalt, manganese, nickel, magnesium, and calcium salts 10 mols.

of water of crystallisation. The asymmetry of the anion is shown by the fact that the strychnine salt is separable into dextro- and lævo-rotatory components. T. H. P.

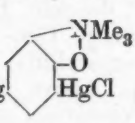
Stable Partial-valency Compounds of Triphenylboron, a Contribution to the Problem of the Valency of Boron. E. KRAUSE (*Ber.*, 1924, **57**, [*B*], 813—818).—Triphenylboron (cf. Krause and Nitsche, A., 1922, i, 694) unites readily with ammonia and with aromatic amines to form well-crystallised additive compounds stable to atmospheric oxygen; they contain 1 mol. of base, the boron having therefore the co-ordination number 4. The stability of the compounds is attributed in large part to steric effects, and also to a species of salt formation due to the acidifying effect of the phenyl groups. The following *compounds*, all of which form colourless crystals, were prepared by adding the requisite amine to triphenylboron in ethereal solution and have the general formula, Ph_3B,R (R=base): R=NH_3, m. p. above 212° (decomp.); R=NH_2Me, m. p. 208—209° (decomp. 210—211°); R=NH_2Et, m. p. 166—168°, decomp. above 200°; R=NH_2Pr^{α}, m. p. 101—102°, decomp. above 180°; R=$NHMe_2$, m. p. 186—187°, decomp. 187—200°; R=NMe_3, m. p. 135—137°; R=NH_2Ph, m. p. 138—140° (decomp.). *Additive products* were obtained (not crystalline) with *ethyl-* and *diethyl-aniline*. R=*pyridine*, decomp. above 214°; R=*quinoline*, m. p. 160—170° (decomp.); R=*quinaldine*, m. p. 110—112° (decomp.); R=*piperidine*, m. p. 213—214°, decomp. above 216°; R=*phenylhydrazine*, $Ph_3B,Ph{\cdot}NH{\cdot}NH_2$, m. p. 138—140°; it is not stable in air indefinitely. Diphenylamine does not combine with triphenylboron. F. A. M.

Factors affecting the Stability of Mercurials and the Mercurisation of Substituted Phenylammonium Salts. M. S. KHARASCH and L. CHALKLEY, jun. (*J. Amer. Chem. Soc.*, 1924, **46**, 1211—1223).—Certain mercuri-organic compounds form a suitable means for testing the hypothesis that the comparative non-labilisation of a chlorine atom, *ortho* or *para* to one or two negative groups (as compared with a similarly situated bromine or iodine atom), may be due to intramolecular oxidation-reduction between the chlorine and carbon atoms, since the grouping –HgX undoubtedly remains positive, and any intramolecular oxidation-reduction is accompanied by the immediate separation of metallic mercury. *3-Dimethylamino-6-acetoxymercuriphenol*, from mercuric acetate and *m*-dimethylaminophenol, in alcoholic solution, forms dirty yellow crystals decomposing with liberation of metallic mercury on storing for 10—14 days. It melts at 100—110° (decomp., with formation of a pink dye). On methylation it affords *3-dimethylamino-6-acetoxymercurianisole hydrochloride*, faintly pink, leaf-like crystals, m. p. 140—150°, decomp. at 190°, to give a pink, fluorescent dye. On boiling a glacial acetic acid solution of mercuric acetate and *m*-dimethylaminophenol, metallic mercury is precipitated, and a mercury-free, pink dye is formed, the *base* of which, $C_{18}H_{22}O_2N_2$, is precipitated by ammonia.

3-*Dimethylamino*-6-*acetoxymercuriphenyl acetate*, similarly prepared from *m*-dimethylaminophenyl acetate, forms colourless crystals, m. p. 110°, which blacken on storing. 4 : 6-*Diacetoxymercuriresorcinoldimethyl ether*, similarly prepared, forms white, feathery crystals, m. p. 218—220°. *Mercuri-bis*-m-*hydroxyphenyltrimethylammonium acetate* (annexed formula), obtained by the



action of mercuric acetate on *m*-hydroxyphenyltrimethylammonium hydroxide, forms a hygroscopic, white powder, m. p. 116—117° (decomp.). On treatment with mercuric chloride in 60% alcohol, it affords m-*hydroxychloromercuriphenyltrimethylammonium anhydride*, $ClHg{\cdot}C_6H_3(NMe_3O)$, as a white solid, m. p. 130—150° (decomp.). 4-*Hydroxy*-3 : 5-*diacetoxymercuriphenyltrimethylammonium acetate* forms colourless needles, m. p. 155—160° (decomp.), which are stable when dry. 4-*Hydroxy*-3-*chloromercuriphenyltrimethylammonium acetate* is obtained from the mother-liquors of the last compound by treatment with sodium chloride, as small, slightly brown needles, m. p. 155—160° (decomp.). 2-*Hydroxy*-3 : 5-*dichloromercuriphenyltrimethylammonium anhydride* (annexed formula), obtained by treating the



product of the reaction between *o*-hydroxyphenyltrimethylammonium hydroxide and mercuric acetate with sodium chloride, forms a white, amorphous solid, m. p. 215—220° (decomp.), after turning violet at 200—210°.

m-Aminophenyltrimethylammonium chloride hydrochloride, $C_6H_4(NMe_3Cl){\cdot}NH_2,HCl$, obtained by heating *m*-nitroaniline hydrobromide with methyl alcohol under pressure at 90—100° and reducing the product, forms pale yellow needles, m. p. 190—200° (decomp.). On treatment with silver hydroxide, it yields the base without decomposition, and this reacts with mercuric acetate with formation of 3-*amino*-4 : 6-*dichloromercuriphenyltrimethylammonium acetate*, colourless crystals, m. p. 200° (decomp.). The times required for blackening to commence when the above compounds are treated with hydrogen sulphide in pyridine or pyridine–water solution are given, and the bearing of these results on the two-stage mercurisation hypothesis of Kharasch and Jacobsohn (A., 1922, i, 189) is discussed. F. G. W.

Hydroferrocyanides and Hydroferricyanides of the Organic Bases. III. W. M. Cumming (*J. Chem. Soc.*, 1924, **125**, 1106—1108).—The hydroferrocyanides obtained from a number of organic bases by precipitation in alcoholic solution are described (cf. T., 1922, **121**, 1287; 1923, **123**, 2457).

Hydroferricyanides have also been produced in acid and neutral alcoholic solutions. Even at −20°, the salts of primary bases oxidise very rapidly. Most secondary bases only give pure salts at low temperatures, whereas tertiary bases yield well-defined salts at the ordinary temperature. The formation of a hydroferricyanide is hindered by the presence of an acidic substituent in the nucleus, except in the case of *p*-bromo- and *p*-nitroso-dimethyl-

aniline; such substituents in a primary amine appear to prevent oxidation. The hydroferricyanides form well-defined crystals which are more highly coloured and more stable than the corresponding hydroferrocyanides previously described (T., 1922, **121**, 1288). The constitution of the salts depends on the acidity of the solution, except in the case of methylaniline. C. J. S.

Halogenated Proteins. II. Bromopeptone. A. J. J. VANDEVELDE (*Rec. trav. chim.*, 1924, **43**, 326—328).—Witte's peptone reacts with bromine in carbon tetrachloride solution, forming *bromopeptone A*, a hygroscopic, yellow powder having an irritating odour and containing 37·55% of bromine. When treated with hot alkali hydroxide solution, it loses bromine corresponding with 33·29% of its weight. At 100°, bromopeptone A undergoes partial decomposition, forming the hygroscopic *bromopeptone C*, containing 30·83% of bromine, and losing 25·61% when warmed with potassium hydroxide solution. Bromopeptone A can be separated into its constituents in the same way as the original peptone; the quantity of albumoses is found to have diminished and the amino acids increased. The precipitates obtained from a solution of the bromopeptone with zinc sulphate or with phosphotungstic acid contain very little bromine (cf. this vol., i, 678). E. H. R.

Nitration of Proteins. I. and II. F. LIEBEN (*Biochem. Z.*, 1924, **145**, 535—554; 555—559).—I. From a quantitative study of the course of nitration of silk-fibrin, casein, and blood-fibrin with concentrations of nitric acid varying from 5 to 60%, it is concluded that in each case the process consists in the formation of the mononitro derivatives of the tyrosine residues, and if tryptophan is also present, as in casein and blood-fibrin, this amino-acid also gives rise to a mononitro derivatve. Nitrofibroin and nitrocasein are reduced to colourless products by hydrogen and sodium hyposulphite in the presence of sodium carbonate. The amino nitrogen of the reduced products determined by Van Slyke's method is the same as that of the nitroproteins (a new amino-protein is therefore not formed on reduction), and slightly greater than that of the original protein, an increase which is ascribed to degradation during nitration.

II. The quantitative course of the nitration of serum-albumin, serum-globulin, lactalbumin, edestin, gliadin, and keratin is in agreement with the supposition (cf. I.) that the mononitro derivatives of the tyrosine and tryptophan present in these proteins are formed. J. P.

Biochemistry.

Blood as a Physico-chemical System. II. L. J. Henderson, A. V. Bock, H. Field, and J. L. Stoddard (*J. Biol. Chem.*, 1924, **59**, 379—431).—A complete description of the changes known to occur in blood during the respiratory cycle and of the physico-chemical system which determines them is given. It has been shown (cf. A., 1921, i, 473) that all external changes in oxygen or carbon dioxide tension are invariably accompanied in blood, not only by changes in free and combined oxygen and carbonic acid concentrations, but also by changes in hydrogen-ion concentration and in the distribution of chlorides between cells and plasma. This study of the physico-chemical system was incomplete, since the movement of water between cells and plasma was left out of account. This factor is now further investigated and it appears that the theory concerning water and chloride distribution as a function of buffer actions of proteins, of alkali reserve, and of osmotic pressure (A., 1909, ii, 157) is valid. All the known phenomena of the respiratory cycle in blood have been described with a good approach to accuracy with the following seven variables: free oxygen, total oxygen, free CO_2, total CO_2, p_H of the serum, the volume of the corpuscles, and the ratio of the concentrations of anions within and without the cell. D. R. N.

Oxygen and Carbon Dioxide Dissociation Curves of Human Blood. A. V. Bock, H. Field, and G. S. Adair (*J. Biol. Chem.*, 1924, **59**, 353—378).—The oxygen dissociation curves for the blood of normal subjects at carbon dioxide tensions varying between 3 and 80 mm. do not conform to Hill's formula (*J. Physiol.*, 1910, **40**, 4). Carbon dioxide dissociation curves on fully reduced and fully oxygenated blood as well as the true plasma curves have also been studied. Both corpuscles and plasma transport carbon dioxide, the former carrying 40% of the total and the latter 60%.
D. R. N.

Chemistry of Hæmoglobin. II. Equilibrium between Oxygen and Hæmoglobin. R. M. Ferry (*J. Biol. Chem.*, 1924, **59**, 295—327).—The equilibrium between oxygen and hæmoglobin has been examined by a method based on a study by purely physical means of the gas phase in equilibrium with hæmoglobin and susceptible of considerable accuracy. A measured volume of hæmoglobin is brought into equilibrium with varying quantities of oxygen in an apparatus having a known volume, so arranged that a portion of the gas phase can be removed and measured without altering the equilibrium in the liquid phase and thus not only the amount of oxygen in the entire gas phase, but also its tension can be calculated through the application of gas laws. The difference between the quantity of oxygen introduced and that in the gas phase corresponds with the amount in combination with hæmoglobin. D. R. N.

Variations in the Acid–Base Balance of the Blood in Disease. V. C. MYERS and L. E. BOOHER (*J. Biol. Chem.*, 1924, **59**, 699—712).—A series of determinations of the p_H and the carbon dioxide content of the venous blood plasma of normal and diseased individuals was made. It was found that in pathological condition the p_H may be within normal limits whilst the carbon dioxide content is abnormal, and *vice versa*, so that the determination of one of these quantities alone is an insufficient index of the state of the acid–base balance. C. R. H.

Effect of Ether added *in vitro* on the Distribution of Carbon Dioxide and Chloride between Cells and Serum. J. H. AUSTIN and H. C. GRAM (*J. Biol. Chem.*, 1924, **59**, 535—541).—Observations on the carbon dioxide and chloride content, the hydrogen-ion concentration, and the relative volume of cells and serum in blood equilibrated at a known tension of carbon dioxide, reveal no change in any of these quantities whether or no ether in anæsthetic concentration is present in the blood. C. R. H.

Changes in the Stability and Potential of Cell Suspensions. II. Potential of Erythrocytes. A. H. EGGERTH (*J. Gen. Physiol.*, 1924, **6**, 587—596).—When erythrocytes from human or sheep blood are washed with physiological salt solution and then suspended in solutions of p_H 5·2 or more acid, they become progressively more electropositive. This change is coincident with hæmolysis, and is, in fact, due to the escape of hæmoglobin from the cells, as in shown by the effect of adding hæmoglobin to a fresh suspension of cells. The isoelectric point of erythrocytes in the absence of salts or in the presence of salts with univalent ions is at p_H 4·7; in the presence of salts with bivalent anions it becomes more acid. C. R. H.

Agglutination of Red Blood Cells. J. H. NORTHROP and J. FREUND (*J. Gen. Physiol.*, 1924, **6**, 603—613).—The agglutination of unsensitised sheep erythrocytes by electrolytes usually occurs when the potential difference between cells and solution is reduced below 6 millivolts; in the case of sensitised cells, the corresponding critical potential difference is about 12 millivolts. It therefore appears that agglutination by immune serum is due to an increase in the critical potential difference and not to a lowering of the actual potential of the cells. C. R. H.

Coloration of so-called " Oxydasic " Granulations of Cells Obtained by Synthesis with Indophenol and Hydroxybenzidine. A. C. HOLLANDE (*Compt. rend.*, 1924, **178**, 1215—1217).—Human leucocytes which take up colouring matters derived from indophenol and hydroxybenzidine do so as a result of that type of dyeing which involves precipitation of the colour. The portions which become coloured are the granulations and also the liquid substances which are formed from or give rise to them. They are not dyed by phenylene-blue or toluylene-blue, and there appears to be no relation between existence of oxydase or peroxydase and power of colour-absorption. H. J. E.

Urea Content of Red Blood Cells. Z. Aszódi (*Biochem. Z.*, 1924, **146**, 343—348).—In the blood of normal individuals the urea is uniformly distributed between corpuscles and plasma, whilst in cases of kidney affections the plasma may contain rather more urea than the corpuscles (cf. Falta and Richter-Quittner, *ibid.*, **100**, 148; Andresen, *ibid.*, **116**, 266). J. P.

Cause of the Rapid Disappearance of Catalase in Blood Solutions. O. Steppuhn and A. Timofejewa (*Biochem. Z.*, 1924, **146**, 108—114).—From measurements of the "protease number" (Bach and Zubkova, A., 1922, i, 392) of dilute blood solutions in the presence of trypsin, it is concluded that the latter has no effect on the protease, as measured by the catalase activity, and that no evidence is forthcoming in support of the view that blood catalase is destroyed by proteases (cf. Wäntig and Steche, *Z. physiol. Chem.*, 1914, **93**, 228). The disappearance of catalase is associated with the presence of erythrocytes, and does not occur in serum. It is not affected by the presence of sodium oleate. In physiological salt solution, the catalase activity first falls rapidly, then rises to normal values. J. P.

Behaviour of the Lipoids of the Blood Immediately after Fat Ingestion in Normal and Diabetic Cases with and without the Administration of Insulin. H. U. Hartmann (*Biochem. Z.*, 1924, **146**, 307—317).—The lipoids of the blood are not affected by the ingestion of dextrose. One hour after the administration of 50 g. of butter and 20 g. of oatmeal to normal and diabetic subjects, a rise in the blood lipoids occurs, but these return to a normal level after 4 hours. The individual components of the lipoid fraction show irregular variations. In one case of diabetes (no acidosis), the blood lipoids were permanently above normal, chiefly due to an increase in neutral fat and cholesterol ester. In three out of four cases of diabetes, insulin slightly depressed the total lipoids of the blood, but no specific effect on any one component was observed. A previous injection of insulin has no effect on the increase of lipoids following the ingestion of butter and oatmeal, and the blood-sugar curve is independent of the lipoid curve. J. P.

Fatty Acids of Blood Plasma. II. Distribution of Unsaturated Acids. W. R. Bloor (*J. Biol. Chem.*, 1924, **59**, 543—556).—A fractionation of the total lipoids of blood plasma indicates that the greater part of the unsaturated fatty acids are present in the form of cholesterol esters; the iodine values of the acids from these esters show that they must include acids of a higher degree of unsaturation than oleic. C. R. H.

Detection of Higher Multiple Unsaturated Free Fatty Acids in Blood. A. von Szent-Györgyi.—(See ii, 508.)

Quantitative Determination of the Free Fatty Acids of Blood. A. von Szent-Györgyi and T. Tominaga.—(See ii. 508.)

Uric Acid Content of the Serum and Spinal Fluid in Children. E. LESNÉ, HASARD, and LANGLE (*Compt. rend. Soc. Biol.*, 1923, **89**, 891—893; from *Chem. Zentr.*, 1924, i, 681).—In the blood-serum of children aged between 3 months and 12 years, the mean uric acid content was found to be 0·0035% as against 0·0049% in the case of the blood-serum of adults. The mean uric acid content of the spinal fluid of children was 0·0018%. In tubercular meningitis no appreciable increase in the uric acid content of the spinal fluid was observed. With meningococcal meningitis, on the other hand, there was a marked increase to 0·0038% of uric acid. G. W. R.

Nuclein Metabolism. II. Isolation of a Nucleotide from Human Blood. H. JACKSON (*J. Biol. Chem.*, 1924, **59**, 529—534).—The precipitate obtained by treating a protein-free filtrate from blood with lead acetate in the presence of acetic acid yielded a substance which gave the reaction for pentoses and from which, after hydrolysis with dilute sulphuric acid, adenine was isolated as the picrate. C. R. H.

Diffusibility of the Calcium of Blood-serum through Collodion Membranes. Effect of Sodium Chloride and Changes in Hydrogen-ion Concentration. R. F. LOEB [with S. STEINBERGER] (*J. Gen. Physiol.*, 1924, **6**, 453—456).—Only 55—75% of the calcium present in serum is dialysable through collodion membranes against distilled water at p_H 7·4, but the whole of the calcium is dialysable against 0·8% sodium chloride solution of p_H 7·4, or against hydrochloric acid of p_H 2·5. W. O. K.

Action of Bicarbonate and Secondary Phosphate on the Dissociation of Calcium. H. BEHRENDT.—(See ii, 456.)

Accurate Determination of Calcium in Whole Blood. A. C. ALPORT.—(See ii, 500.)

Micro-determination of Methyl Alcohol in Blood. N. V. BILDSTEN.—(See ii, 506.)

Coagulation of Blood. J. AMAR (*Compt. rend.*, 1924, **178**, 1628—1630; cf. this vol., ii, 144).—Further experiments show the bearing on the coagulation of blood of those physico-chemical factors which determine the coagulation of colloids by depressing the surface tension of the medium. Coagulation of blood is due to the disturbance of the equilibrium of its components resulting from a fall in the surface tension. This may be due to the action of a solid partition which is moistened by water, and to the standing of the blood, this causing separation of the components of the emulsion in the order of their densities, so that the solubilising salts of the supernatant liquor leave the corpuscles free to precipitate. Addition of salts, alcohols, or poisons capable of coagulating the proteins hastens the formation of the clot. Coagulation exhibits also an enzymic aspect, the diminution in the surface

tension liberating the fibrin-coagulating enzyme of the leucocytes; that this is the case is shown by the observation that the production of filaments begins round the white corpuscles.

The view that sodium salts have anti-coagulating properties only because they precipitate the calcium salts is inaccurate, sodium carbonate, chloride, and phosphate being true anti-coagulants. Further, excess of calcium chloride exerts a toxic action on the leucocytes, shrivelling and coagulating their protoplasm and preventing the discharge of the fibrin enzyme and hence the coagulation of the blood; such effect is the opposite of that usually attributed to calcium chloride. T. H. P.

Lipolytic Theory of Immune Hæmolysis. R. BRINKMAN and A. VON SZENT-GYÖRGYI (*Biochem. Z.*, 1924, **146**, 212—216).—Immune hæmolysis of blood by the addition of amboceptor and complement is not associated with liberation of higher fatty acids. After complete complement-fixation, the lipolytic activity of the serum is undiminished, and it is concluded that complement is not identical with blood lipase (cf. Olsen and Goette, *ibid.*, 1920, **112**, 188). Normal erythrocytes after reversal of hypotonic hæmolysis (*J. Physiol.*, 1923, **58**, 204) show immune hæmolysis, but reversal is not possible after the latter process. Amboceptor and complement are active in blood hæmolysed by hypotonic saline. J. P.

Formation of Porphyrin from Sulphur-Hæmoglobin. P. LIST (*Z. physiol. Chem.*, 1924, **135**, 95—107; cf. Schumm, A., 1923, i, 631).—The author has prepared porphyrins from blood treated with hydrogen sulphide (sulphur-hæmoglobin) by the action of hydrochloric acid. Weak acids, such as phosphoric and acetic acids, are also able to produce colouring matters of the porphyrin type. The products closely resemble the better known porphyrins in absorption spectra, but differ from them in being readily soluble in chloroform. E. M. C.

Determination of Hydrogen Ions in the Gastric Contents. J. F. MCCLENDON (*J. Biol. Chem.*, 1924, **59**, 437—442).—A fairly accurate and rapid method is described for the determination of the p_H of the gastric juice based on the colorimetric determination of the percentage dissociation of quinaldine-red. D. R. N.

Polarimetric Observations on Solutions of Glucose after Contact with Intestinal Mucosa. H. V. HUME and W. DENIS (*J. Biol. Chem.*, 1924, **59**, 457—464).—In order to prove the transitory formation of γ-glucose in glucose solutions after contact with intestinal mucosa, experimental technique other than that involving the use of the polarimeter will have to be employed (cf. A., 1920, i, 508, 648). Although this method gives unmistakable evidence of the existence of mutarotation, it could scarcely be ascribed to the formation of γ-glucose, as in some experiments an increase and in others a decrease in the rotation are observed. D. R. N.

Inorganic Substances in Carbohydrate Metabolism. G. A. HARROP and E. M. BENEDICT (*J. Biol. Chem.*, 1924, **59**, 683—697).—During a period of active assimilation of carbohydrate there is a lessened excretion of phosphate; coincidently with this, there is a reduction of the concentration of inorganic phosphate in the blood-serum and an increase in its concentration in the muscle-tissue. These results are in favour of the view that inorganic phosphate is a necessary intermediate in the storage of carbohydrate as glycogen. C. R. H.

Formation and Origin of Acetaldehyde in the Intermediate Cellular Metabolism of Warm-blooded Animals. C. NEUBERG and A. GOTTSCHALK (*Biochem. Z.*, 1924, **146**, 164—184).—The presence of acetaldehyde—originating from glycogen—in the surviving cells of guinea pig liver pulp can be demonstrated by the use of calcium hydrogen sulphite, and the acetaldehyde may be determined quantitatively by alkalimetric titration using hydroxylamine sulphate (Sieber, *Chem.-Ztg.*, 1921, **45**, 349). The amount of acetaldehyde formed is increased by the addition of sugars and other related substances, and is greatly increased if insulin be added simultaneously. The activity in forming acetaldehyde diminishes in the following order: glycogen, *dl*-glyceraldehyde, zymophosphate, hexose monophosphate, dihydroxyacetone, glycollaldehyde, *d*-fructose, *d*-glucose, whilst from the following compounds the yields of aldehyde also diminished in the order: ethyl alcohol, alanine, *d*-mannitol, *dl*-glyceric acid, glycerol, and glycerophosphoric acid. J. P.

Separation and Identification of Acetaldehyde Formed in the Intermediary Metabolism of Surviving Cells of Warm-blooded Animals. C. NEUBERG and A. GOTTSCHALK (*Biochem. Z.*, 1924, **146**, 185—187).—The identity of the acetaldehyde obtained as the calcium sulphite compound in investigating the metabolism of surviving cells of the liver (cf. preceding abstract) is established by the isolation and analysis of the crystalline *p*-nitrophenylhydrazone (m. p. 128°). J. P.

Some Oxidation Processes of Normal and Cancer Tissue. A. FLEISCH (*Biochem. J.*, 1924, **18**, 294—311).—Glutathione has the same effect with thermostable sarcoma residue as with thermostable muscle residue. Unwashed sarcoma tissue reduces methylene-blue more slowly than muscle. The total amount of oxygen taken up is greater for sarcoma tissue, although it shows a lower initial velocity of oxygen uptake than muscle. Hydrogen cyanide inhibits the oxygen uptake, but not the methylene-blue reduction of unwashed tissue in both cases. Citric acid accelerates the methylene-blue reduction of washed muscle, but not of washed sarcoma. Cyanide has no influence. Muscle as well as sarcoma oxidises citric acid in the Barcroft apparatus. This oxidation is not sensitive to hydrogen cyanide. The most favourable reaction for it is p_H 6·0. Glutamic acid is oxidised by washed muscle and

sarcoma in presence of methylene-blue; lactic acid, on the other hand, is less actively oxidised by sarcoma than by muscle. Fumaric, maleic, and malic acids are not oxidised in this way by either tissue. Succinic acid is oxidised freely whether in the presence of methylene-blue or oxygen, and muscle is the more active of the two in this respect. The quantity of oxygen used corresponds with 1 atom of oxygen for 1 mol. of succinic acid. Whilst hydrogen cyanide has no effect on the methylene-blue reduction, the oxygen uptake by succinic acid is inhibited by it. The oxidation of succinic acid with oxygen can in the case of muscle be restored if methylene-blue is added to the system. This indirect oxidation of succinic acid induced by the methylene-blue occurs to a much less extent in the case of sarcoma. There is evidence that a "hydrogen transport factor" exists which is of importance for the transport of hydrogen to methylene-blue. The factor is distinct from "succinoxydase," and can be washed out. Its concentration is much smaller in sarcoma than in muscle-tissue. The mechanism of the aërobic oxidation of succinic acid is discussed. S. S. Z.

Biological Oxidation. I. Absorption of Oxygen by the System Linoleic Acid–SH Group. A. von Szent-Györgyi.—(See this vol., i, 708.)

Biological Oxidation. II. Mechanism and Significance of SH-Catalysis. A. von Szent-Györgyi.—(See this vol., i, 708.)

Effect of Exercise in Diabetes. I. H. E. Himwich, R. O. Loebel, and D. P. Barr (*J. Biol. Chem.*, 1924, **59**, 265—293).—Following short periods of vigorous exercise in the diabetic, there are changes in acid–base equilibrium somewhat greater than in normal individuals doing a comparable amount of work, as is apparent from a reduction of CO_2 capacity, CO_2 tension, and alkalinity of arterial blood. There is a marked increase of lactic acid and the reduction of CO_2 capacity can be quantitatively accounted for by this increase. After exercise for short periods, no significant change in the concentration of acetone compounds could be observed. The accumulation of lactic acid in the blood of diabetics after exercise indicates that the conversion of carbohydrate into lactic acid is employed as the chemical mechanism of muscular contraction. D. R. N.

Mechanism of the Action of Insulin. The Carbohydrate Balance in Avitaminosis. A. Bickel and J. A. Collazo (*Deuts. med. Woch.*, 1923, **49**, 1408—1410; from *Chem. Zentr.*, 1924, i, 685).—The liver and muscles of pigeons suffering from avitaminosis are practically free from glycogen and the blood-sugar is above normal. Insulin decreases the blood-sugar content and with repeated injections and subsequent administration of sugar recovery takes place. The liver and muscle contain glycogen 6 hours after injection of insulin, whilst the content of fats and amino-acids in the blood falls. The effect of a single injection

of insulin disappears after 24 hours. Insulin appears to facilitate the storage of glycogen. G. W. R.

Changes in the Ionic Content of the Blood after Administration of Insulin. H. STAUB, F. GÜNTHER, and R. FRÖHLICH (*Klin. Woch.*, 1923, **2**, 2337—2338; from *Chem. Zentr.*, 1924, i, 685). —After administration of large doses of insulin to normal dogs and to dogs suffering from diabetic coma, decrease of acidosis, increase of p_H, and increase of the content of sodium, potassium, calcium, and magnesium occur. A marked decrease in inorganic phosphorus in the blood is noted. G. W. R.

Cholesterol Synthesis in the Animal Body. H. BEUMER and F. LEHMANN (*Z. ges. Exp. Med.*, 1923, **37**, 274—280; from *Chem. Zentr.*, 1924, i, 684).—Newly-born dogs fed for 4 weeks on a diet poor in cholesterol, showed an increase in cholesterol in 4 weeks amounting to 20 times the amount of cholesterol administered in the food. The formation of cholesterol therefore probably takes place exclusively from constituents not found in the ether extract of the food substances. G. W. R.

Nitrogen Metabolism in Avitaminosis. J. A. COLLAZO (*Biochem. Z.*, 1924, **145**, 436—441).—In dogs, the urinary purine nitrogen, uric acid, allantoin, ammonia, and amino-acids increase slightly with progressive avitaminosis, but shortly before death they may fall. The variations in uric acid and allantoin are sometimes parallel, sometimes divergent. Urea shows a continuous diminution in avitaminosis, whilst the urinary phosphates are normal in the initial stages, but increase with decreasing body-weight during the late stages. The residual nitrogen of the blood may remain normal for some time, but has a slight tendency to increase. Blood urea behaves in a similar way, whilst the amino-acids of the blood show a slow increase, which becomes more marked in advanced avitaminosis. The increase in the residual nitrogen of the blood is conditioned more by the amino-acids than by urea. It is concluded that in avitaminosis nitrogen metabolism is not disturbed so quickly as carbohydrate and fat metabolism. J. P.

Amino-acids in Nutrition. VIII. Proline. B. SURE (*J. Biol. Chem.*, 1924, **59**, 577—586).—Rats show a marked increase in the gain in weight per gram of protein intake on the addition of proline to a diet composed of edestin together with cystine and lysine. This effect was not obtained with an equivalent amount of pyrrolidonecarboxylic acid. It is concluded that proline is essential for growth. C. R. H.

Synthesis of Amino-acids in the Animal Organism. III. Cystine. J. A. MULDOON, G. J. SHIPLE, and C. P. SHERWIN (*J. Biol. Chem.*, 1924, **59**, 675—681).—The fact that bromobenzene is detoxicated in the animal body by conjugation with cysteine, to form *p*-bromophenylmercapturic acid, was utilised to test the

ability of the dog to synthesise cystine. It was found that only when cystine was fed was there a synthesis of *p*-bromophenylmercapturic acid; neither the cystine of the tissues of the animal itself nor sulphur in other forms in the diet could be utilised for this purpose. C. R. H.

Cystine Deficiency and Vitamin Content of the Lentil, (*Lens esculenta*). D. B. Jones and J. C. Murphy (*J. Biol. Chem.*, 1924, **59**, 243—253).—The proteins of the lentil, like those of beans, are inadequate for nutritive purposes because of their deficiency in cystine and are further characterised by a form of indigestibility which can be corrected by cooking, although the effect of cooking is much less marked in the case of the lentil than in that of other legumes. The vitamin-*A* and vitamin-*B* contents of lentils appear to be much higher than in most other seeds. D. R. N.

Metabolism of Sulphur. VII. Oxidation of Sulphur Compounds Related to Cystine in the Animal Organism. VIII. Behaviour of Thiophenol and Thiocresol in the Animal Organism. R. M. Hill and H. B. Lewis (*J. Biol. Chem.*, 1924, **59**, 557—567, 569—575).—VII.—After administration of the sodium salts of thiolactic and thioglycollic acid to rabbits, either subcutaneously or orally, practically all the sulphur is eliminated in the urine in the first day, 50—70% of it being in the form of inorganic sulphate. Under similar conditions, the sulphur of thiodiglycollic acid is excreted in the unoxidised form.

VIII.—Thiophenol and *p*-thiocresol when administered to rabbits are absorbed only to a small extent; the sulphur is excreted entirely in the unoxidised form.

The authors suggest that in order that a sulphur compound may be susceptible of oxidation in the animal body, the sulphur must be present in an aliphatic mercapto group, or must be able to be transformed into such a condition. C. R. H.

Experiments upon Vitamin-*A*. H. C. Sherman and M. M. Kramer (*J. Amer. Chem. Soc.*, 1924, **46**, 1055—1063).—Young rats (4 weeks) placed on a diet devoid of vitamin-*A*, but adequate in all other respects for healthy nutrition, showed very different growths and survival periods, depending on the food eaten previous to the experimental period. It is suggested that the stores of vitamin-*A* in the bodies of the animals experimented on seriously vitiate the value of much of the earlier work on this subject. Vitamin-*A* was shown to be stored at later ages, and the length of time adult animals can survive on a diet devoid of it, but otherwise adequate, also depends on the amount of this vitamin stored in the body and is an indication of the relative amounts contained in earlier diets. A. C.

Experimental Rickets in Rats on a Purified Synthetic Diet Deficient in Phosphorus and Fat-soluble Organic Factor. H. Goldblatt (*Biochem. J.*, 1924, **18**, 414—418).—The addition to a purified synthetic diet low in phosphorus and the fat-soluble organic factor of calcium carbonate in such an amount that the

proportion of calcium to phosphorus was raised from 1 : 0·88 to 1 : 0·20 had the effect of changing the diet from a non-rickets-producing to a rickets-producing one. S. S. Z.

Remarks on Papers of W. R. Hess and K. Rohr, "The Action of Thermal Treatment of Dry Yeast, etc., and Avian Beriberi," and of Roelli, "The Activation of *in vitro* Respiration by Muscle Juice, etc." E. ABDERHALDEN (*Z. physiol Chem.*, 1924, **134**, 97—99; cf. *Z. physiol. Chem.*, 1923, **192**, 268, 284).—Polemical. W. O. K.

Necessary Conditions for Testing with the Reagent for Vitamin-*C*. (Answer to H. D. Kay and S. S. Zilva.) N. BEZSSONOFF (*Biochem. J.*, 1924, **18**, 384—386).—Polemical. S. S. Z.

Supposed Influence of Irradiated Air on Growth. T. A. WEBSTER and L. HILL (*Biochem. J.*, 1924, **18**, 340—346).—The authors cannot confirm Hume and Smith's results regarding the growth-promoting effects of irradiated air (cf. A., 1923, i, 728). S. S. Z.

Influence of Cell Salts on Intermediate Metabolism. K. TADENUMA (*Biochem. Z.*, 1924, **145**, 481—491).—Dogs kept on a diet containing only sodium chloride as salt component, but otherwise adequate, show a diminution in body-weight, an increase in the residual nitrogen of the blood, and in general an increase in the blood-sugar compared with similarly fed animals receiving an artificial cell salt mixture. The neutral fat of the blood has a slight tendency to increase. In dogs kept on an insufficient diet, substitution of sodium chloride for the salt mixture accentuates the disturbances in metabolism. In general, it is concluded that dogs receiving a diet of adequate calorie value but insufficient in salts exhibit symptoms similar to those of avitaminosis. J. P.

Presence of Silicon in Tissues. L. ISAACS.—(See ii, 499.)

Importance of Zinc in the Feeding of Animals. G. BERTRAND and B. BENZON (*Ann. Inst. Pasteur*, 1924, **38**, 405—419).—A more detailed account of work already published (A., 1922, i, 893).

Part Played by Iron and Fat in the Recovery of Rats from Chronic Experimental Anæmia. J. M. D. SCOTT (*Biochem. J.*, 1924, **18**, 347—350).—Rats were cured from subchronic anæmia by the administration of ferrous chloride when fed on diet of bread and whole milk. When the whole milk was replaced by skimmed milk and palm kernel oil the iron salt had no curative action. S. S. Z.

Method for Estimating the Retention of Calcium and Phosphorus in Young Growing Rats. M. A. BOAS (*Biochem. J.*, 1924, **18**, 425—432).—A method for estimating the retention of calcium and phosphorus in young growing rats for periods of 3 to 7 weeks is described. Rats on normal diet showed a retention which declined week by week, and smooth curves plotted from the figures obtained were similar in shape to the curve of normal growth. S. S. Z.

Mechanism of Vital Staining with Basic Dyes. M. McCUTCHEON and B. LUCKE (*J. Gen. Physiol.*, 1924, **6**, 501—507).—The degree of staining obtained with basic dyes in living cells was compared in solutions containing ammonium hydroxide, sodium hydroxide, carbon dioxide, and hydrochloric acid. A greater degree of staining was obtained in a solution of sodium hydroxide than in one of ammonium hydroxide of the same p_H, which means that with constant extracellular reaction staining is hindered by intracellular alkalinity. With constant intracellular reaction, it is found that staining is favoured by increased extracellular alkalinity. C. R. H.

Basic Peptones from the Mucous Membrane of the Stomach. K. FELIX (*Z. physiol. Chem.*, 1924, **135**, 175—179).—The mucous membrane of the stomach of pigs gives on extraction with cold water peptones of a strongly basic character. These contain considerable quantities of the hexone bases, arginine, histidine, and lysine. They give the biuret reaction and generally the diazo-reaction and are very hygroscopic. E. M. C.

Animal Urease. O. STEPPUHN and X. UTKIN-LJUBOVZOV (*Biochem. Z.*, 1924, **146**, 115—121).—The livers of the dog and horse contain a small amount of urease, which is better detected in acid extracts than in the expressed juice from the organ. It is probably derived from vegetable sources. It is not mobilised during acidosis for the purpose of neutralising acidity, and it is concluded that it is devoid of physiological significance. J. P.

Autolysis. II. P. RONA and E. MISLOWITZER (*Biochem. Z.*, 1924, **146**, 1—25).—The autolysis of guinea pig liver pulp at the optimum p_H 3·6 is inhibited by sodium chloride, bromide, sulphate, citrate, and tartrate in 0·2*M* concentration, whilst sodium acetate is inactive. At p_H 5—6·0, the action of these salts is reversed and autolysis is increased. The cations sodium, potassium, and calcium at p_H 3·6, in concentrations of from 1·0 to 0·5*N*, inhibit, and in concentrations between 0·25 and 0·1*N* increase autolysis. Within the former range of concentrations, sodium has a more marked inhibitory effect than potassium, whilst in the latter range potassium increases autolysis more than sodium. Calcium, in concentrations between 1·0 and 0·1*N*, has a greater increasing and a lesser inhibiting action than potassium. In 0·05*N* solution, the order of activity in increasing autolysis is Na>K>Ca. At p_H 5·0, a reversal of action, similar to that of the anions, is also observed in the case of the cations. Lithium and rubidium increase autolysis to a less extent than does sodium. J. P.

Autolysis. III. Autolysis of Phosphorus-poisoned Liver. P. RONA, E. MISLOWITZER, and S. SEIDENBERG (*Biochem. Z.*, 1924, **146**, 26—35).—The autolysis of a phosphorus-poisoned guinea pig liver is greater than that of the normal liver. This is ascribed to the gradual increase in the hydrogen-ion concentration, since if the pulp be buffered at the optimum p_H 3·6 or at higher p_H, the extent of autolysis observed is normal. In the buffer-poisoned liver, the

autolysis products have amino-nitrogen values from 70 to 100% higher than the normal. J. P.

Chemistry of Gaucher's Disease. E. EPSTEIN (*Biochem. Z.*, 1924, **145**, 398—414).—A histo-chemical and qualitative investigation of the "Gaucher substance" found in the cell vacuoles of the spleen from cases of Gaucher's disease. It is concluded that this substance is not homogeneous, and its formation is associated with a diminution in the nitrogen and an increase in the carbohydrate of the spleen. The ethereal extract of the affected spleen does not differ qualitatively or quantitatively from that of the normal organ, whilst the alcoholic extract, when precipitated with mercuric chloride, yields a colourless, micro-crystalline, phosphorus-free substance, m. p. 176°, capable of swelling in water, with the physical and chemical properties of a sphingogalactoside. The presence of such a substance is not demonstrable in the normal spleen. J. P.

Creatine and Creatinine in Muscle Extracts. F. S. HAMMETT (*J. Biol. Chem.*, 1924, **59**, 347—351).—Creatine is formed from creatinine in muscle tissue or its extracts on incubation or autolysis. The rate of this transformation is practically the same in extracts of brain- and muscle-tissues, when the two extracts are obtained from tissues from the same animals using Tyrode's solution as the extraction agent and phosphate mixture as buffer during simultaneous aseptic incubation at 37—38°. This rate is twice as great as that in buffered Tyrode's solution. It is further shown that in the brain, as in the muscle, there are no enzymes which produce creatine or which destroy creatinine or creatine. It is concluded that creatinine formation occurs in brain as well as in muscle, thus supporting Folin's view that creatinine formation is a function of the total normal tissue metabolism. D. R. N.

Succinic Acid in Muscle. I. D. M. MOYLE (*Biochem. J.*, 1924, **18**, 351—364).—Fresh ox muscle yields a small quantity of succinic acid. This yield is increased when the muscle of the ox, dog, sheep, rabbit, and possibly frog is incubated anaërobically in a phosphate buffer solution of p_H 7·0—8·4. A bigger yield of the acid is also obtained if glutamic or aspartic acid is added. The addition of sugar does not alter the yield, whilst the addition of certain pancreatic preparations markedly decreases it. In the red muscle of the rabbit a greater yield is obtained than in the white. A method for the determination of succinic acid is described. It is based on the volumetric determination of the silver in the silver succinate precipitate of the muscle extract after the removal of all other interfering constituents. S. S. Z.

Distribution and Variation of Carnosine in Cat Muscle. G. HUNTER (*Biochem. J.*, 1924, **18**, 408—411).—The carnosine content of various muscles in a number of cats has been ascertained. In the same animal, carnosine is a variable constituent of white muscle, but is approximately constant in red. S. S. Z.

Testing for Incipient Putrefaction [of Foodstuffs]. J. Tillmans and R. Otto (*Z. Unters. Nahr. Genussm.*, 1924, **47**, 25—37).—The flesh of fish decomposes differently from that of mammals. Incipient decomposition of fish can be detected by determining the ammonia and amino-acid nitrogen, although this method fails to indicate the incipient decomposition of meat. Fish containing more than 0·03% of ammonia or more than 0·1% of amino-acid nitrogen, as determined by methods the details of which are given, may be considered to be in a state of incipient decomposition. Other methods of detecting incipient decomposition of fish, depending on the content of amino-acids and polypeptides, on oxygen absorption, and on the reduction of potassium nitrate and of methylene-blue, are described. The identification and determination of peptones, carbonic acid, indole, soluble nitrogen, and substances combining with iodine lead to uncertain or negative results and no new method of indicating the incipient decomposition of fish could be founded on these substances as criteria.

H. C. R.

Proteolytic Enzymes in the Thymus. G. Widmark (*Z. physiol. Chem.*, 1924, **135**, 122—128).—The soluble products of autolysis of acidified calf thymus contain enzymes showing optimum activity at p_H 5·6 and 7·6, respectively, comparable to those obtained by Hedin (A., 1923, i, 507) from milk, lymphatic glands, and kidney and by Zachrisson (*Upsala Läkaref förhandl.*, 1923, **28**, 333) from the liver. The insoluble products give a sodium chloride extract containing an enzyme with an optimum at about p_H 8·0.

E. M. C.

Reduction of Sodium Nitrate and Potassium Chlorate during the Putrefaction of Viscera. C. Ghigliotto (*Ann. Falsif.*, 1924, **17**, 93—95).—Sodium nitrate and potassium chlorate are reduced rapidly during the putrefaction of animal organs.

W. P. S.

Reduction of Aromatic Nitro Groups by the Tissue of Guinea Pigs after Treatment with Proteins and during Anaphylactic Shock. IX. The Effect of Proteins. H. Löhr (*Z. ges. exp. Med.*, 1923, **37**, 442—453; from *Chem. Zentr.*, 1924, i, 682).—The ability of isolated cells to reduce nitro groups, *e.g.*, in *m*-dinitrobenzene, can be increased by preliminary administration of milk and serum. The greatest activation was produced in the kidneys, followed by the muscles and the brain. The liver was practically unaffected. Peptone injection decreased reducing power. The same effect was also shown by peptone on muscle cells *in vitro* and also during anaphylactic shock.

G. W. R.

Carotin. The Principal Cause of the Red and Yellow Colours in *Perillus bioculatus* (Fab.) and its Biological Origin from the Lymph of *Leptinotarsa decemlineata* (Say). L. S. Palmer and H. H. Knight (*J. Biol. Chem.*, 1924, **59**, 443—449).—The yellow and red colours of the hypodermis of the stink-bug, *Perillus bioculatus* (Fab.), are due largely to carotin, which is

derived from the food, chiefly the lymph of the potato-beetle, *Leptinotarsa decemlineata* (Say). The lymph of the potato-beetle is coloured exclusively by carotin, amounting to 0·0136% in the fresh lymph, which is about the same concentration as that found in fresh green leaves. Experiments showing that the amount of carotin deposited in the hypodermis of insects can be permanently modified by environment without removing the source of pigment require substantiation before they may be accepted as illustrating the inheritance of acquired characters. D. R. N.

Anthocyanin and Flavone-like Pigments as Cause of Red Colorations in the Hemipterous Families, *Aphididæ*, *Coreidæ*, *Lygæidæ*, *Miridæ*, and *Reduviidæ*. L. S. Palmer and H. H. Knight (*J. Biol. Chem.*, 1924, **59**, 451—455).—Red pigment in both phytophagous and predaceous families of Hemiptera is not limited to one type of substance, as water-soluble pigments appear to be more common than carotin. The aphid, *Tritogenaphis rudbeckia*, owes its vermilion colour chiefly to an anthocyanin-like pigment, although small quantities of carotin are also present. The red colour of the red and black patterned phytophagous box-elder plant-bug and other bugs is due to a flavone-like pigment. From these results it is difficult to understand how environment can cause a permanent modification of an insect colour pattern involving an animal pigment which is derived from the food and is subject to fundamental physiological processes of the protoplasm without first causing a permanent modification of the processes to which the derived pigment is subject. The view that the red pigment in insects can thus be modified and the modification become inheritable is weakened in the light of these findings that the pigment is likely to be a carotinoid, anthocyanin, or flavone derived from food. D. R. N.

Composition of Herring Roe. VI. Monoamino-acids of Ichthulin. K. Iguchi (*Z. physiol. Chem.*, 1924, **135**, 188—197; cf. Steudel and Takahashi, A., 1923, i, 729, 1257).—A fractionation of the monoamino-acids of ichthulin, the protein from herring eggs, has completed the data necessary for showing the fundamental identity of the protein in the ripe eggs and in the empty egg casing. E. M. C.

Gases of the Air-bladder of *Porichthys notatus*. C. W. Greene (*J. Biol. Chem.*, 1924, **59**, 615—621).—The oxygen content of the gas from the air-bladder of this fish ranges from 30% to 88·2%; the carbon dioxide from 0 to 2·4%; the nitrogen from 4·8% to 70%. The gas obtained after the bladder has refilled is not markedly different from the first sample. C. R. H.

Echinococcal Anaphylaxis. J. H. Botteri (*Z. ges. exp. Med.*, 1923, **37**, 175—183; from *Chem. Zentr.*, 1924, i, 682).—In echinococcal infections the hydatid fluid contains albuminoid and lipoid substances. The proteins, separated by salting out with sodium chloride and redissolved, give the anaphylactic reaction with the diseased animals. The reaction is still given after removal of

coagulable proteins from the solution. Hydatid fluids, from oxen, giving no sulphosalicylic acid or biuret reaction and giving only a positive "ninhydrin" reaction, are found to be biologically active. The intensity of the reaction is correlated with protein content. Of the proteins isolated, euglobulins give the strongest reaction, followed by the pseudoglobulins. The albumins are scarcely reactive. Lipoids and products of protein hydrolysis do not produce anaphylaxis. The positive intracutaneous reaction given by hydatid fluid appears to be associated either with the presence of small amounts of protein which can be detected serologically but not chemically, or with the presence of differently constituted substances having anaphylactic properties.

G. W. R.

Acetaldehyde Content of the Urine in Normal and Pathological Conditions. W. STEPP and I. ROTHMAN-MANHEIM (*Biochem. Z.*, 1924, **146**, 349—360).—In normal urines the amount of acetaldehyde excreted (2—4 mg. in 24 hours) is not influenced by withholding carbohydrates from the dietary nor by starvation, from which it is concluded that the formation and excretion of the aldehyde is not related to that of acetone. In cases of nephritis, nephrosis, uræmia, in liver affections, and in various other pathological conditions, no significant variations in acetaldehyde excretion were observed, whilst in cases of diabetes insipidus this was markedly increased (16—27 mg. per diem). Excretion of acetaldehyde is not of constant occurrence in diabetes, being most marked in, whilst showing no parallelism to, advanced glycosuria with associated ketonuria, but falling off in acidosis and in coma. As in normal cases, the excretion of acetaldehyde is not influenced by dietetic conditions. J. P.

Excretion of Amino-acids by Infants during Starvation and on a Protein-rich Diet. Formol Titration in Small Quantities of Urine. F. VON BEMUTH and F. GOEBEL (*Biochem. Z.*, 1924, **146**, 336—342).—In a newly-born child with a closure of the œsophagus and therefore unable to feed, abnormally high amino-nitrogen values were found in blood and urine. This is ascribed to an impairment of de-aminising powers induced by starvation. From feeding experiments in normal infants, the high amino-nitrogen excretion is ascribed to the high permeability of the kidney to amino-acids, a condition dependent to a certain extent on diet. Improvements in the Sörensen method of formol titration are described which render the process more readily applicable to small quantities of urine. J. P.

Are Guanidines Present in the Urines of Parathyroidectomised Dogs? I. GREENWALD (*J. Biol. Chem.*, 1924, **59**, 329—337).—The author's experiments did not afford conclusive evidence of an increased formation or decreased destruction of guanidines after parathyroidectomy, nor did they prove the absence of guanidines from the urines of parathyroidectomised dogs. There are only two well authenticated metabolic changes after parathyroidectomy,

viz., lowered calcium content of serum or plasma, and diminished excretion of phosphorus in the urine. D. R. N.

Proteinogenous Amines. XVI. Excretion of Iminazoles in the Urine. K. K. KOESSLER and M. T. HANKE (*J. Biol. Chem.*, 1924, **59**, 803—834).—If urine be treated with lead acetate and sodium hydroxide, all the iminazole compounds are left in the filtrate. A series of determinations by the colorimetric method shows that the normal daily excretion of these compounds is between 120 and 220 mg. In cases of nephritis with nitrogen retention, the daily excretion is definitely lower than in the normal person on the same diet. C. R. H.

Urinary Hydrogen-ion Concentration in Normal Man during Fasting. LE NOIR and A. M. DE FOSSEY (*Compt. rend.*, 1924, **178**, 1632—1633).—During fasting, the value of p_H for human urine normally undergoes only very slight variation, but falls slightly if the subject indulges in prolonged muscular effort. T. H. P.

Relation of the Alkaline-earth Metals to the Acidity of Urine. L. LESCŒUR and L. MOQUET (*Compt. rend. Soc. Biol.*, 1923, **89**, 1036—1038; from *Chem. Zentr.*, 1924, i, 682).—Acidity in urine may be correlated with high specific gravity and high content of alkaline-earth and other salts. The elimination of magnesium in urine increases with the acidity. Calcium shows a less close relationship. G. W. R.

Colloids in the Urine and the Blood. J. WOHLGEMUTH and T. KOGA (*Biochem. Z.*, 1924, **146**, 36—51).—The property of frothing shown by urine is ascribed to the presence of a positively charged colloid, since the property is lost by shaking the urine with kaolin but not with aluminium oxide. Starvation increases the amount of this colloid in the urine. If the urine be dialysed, the foam-forming colloid loses its positive charge and becomes amphoteric, a result which is ascribed to the removal of the cations which are responsible for the charge. The colloid is not affected by boiling or by low temperature (−12°), nor is its presence related to the surface tension of the urine. It contains nitrogen, and its particles have a size of 1 μ. Nephritic and icteric urines contain more of the colloid than normal urines. A similar foam-forming colloid is present in blood-sera, notably in nephritic sera, but it has a negative charge. Aqueous suspensions of blood-corpuscles foam but slightly on shaking, but on acidification with acetic acid this property is much increased. It is not influenced by kaolin or alumina. J. P.

Effect of Metallic Salts on the Bactericidal Action of Blood-plasma. L. E. WALBUM (*Compt. rend. Soc. Biol.*, 1923, **89**, 1007—1010; from *Chem. Zentr.*, 1924, i, 681).—On addition of one drop of a 24-hour bouillon culture of *Bacillus coli* to fresh citrate plasma containing different metallic chlorides, the first effect with incubation at 37° was a diminution in bacterial numbers, followed

eventually by an increase so that after 2 hours bacterial numbers were greater than originally. Considering the effect in the first period, it was found that with salts of calcium, magnesium, silver, ferric salts, and chromic salts the bactericidal effect increased with decreasing atomic weight. The reverse held for the platinum group, and for cobalt, nickel, and manganese. Intravenous injection of manganous chloride increased the bactericidal action of the blood in the case of a goat. G. W. R.

Poisoning from Barium Sulphate in an *X*-Ray Examination. E. DINSLAGE and F. BARTSCHAT (*Z. Unters. Nahr. Genussm.*, 1924, **47**, 7—9).—A case of fatal barium poisoning due to the presence of barium carbonate in a sample of barium sulphate administered previous to an *X*-ray examination is described. H. C. R.

Action of Thorium-*X* on the Maturation of Eggs, the Germination of Seeds, and the Growth of Plants. AVERSENQ, DELAS, JALOUSTRE, and MAURIN (*Compt. rend.*, 1924, **178**, 1491—1492).—Experiments with eggs of *Ascaris lumbricoides* show that small doses of thorium-*X* increase the rate of maturation whilst larger doses much retard it. Similar effects are observed on the germination of seeds of *Raphanus*, and the growth of *Lemna polyrrhiza*. A. B. H.

Uranium Diuresis. R. HEILIG (*Z. ges. exp. Med.*, 1923, **37**, 163—174; from *Chem. Zentr.*, 1924, i, 684).—Subcutaneous injection of 3—15 mg. of uranium nitrate produced intense diuresis in dogs without, apart from a short period, increasing the output of sodium chloride. In the initial stages, loss of water from the blood took place accompanied by increase in hæmoglobin, erythrocytes, and residual nitrogen. In the later stages of diuresis, these effects disappeared. The effect of uranium nitrate appears to be principally on the kidneys, but extra-renal factors may also be involved. G. W. R.

Drug Resistance of Trypanosomes. C. VOEGTLIN, H. A. DYER, and D. W. MILLER (*J. Pharm. exp. Ther.*, 1924, **23**, 55—86).—A strain of trypanosomes resistant to arsenic may be produced by inoculating an animal which has previously been treated with an arsenical drug of a type which is slowly excreted; this resistance can be reduced by passing the strain through another host. Only arsenic in a compound of the type R·As:O is toxic to trypanosomes *in vitro*, and the toxicity of this type of arsenic compound is completely inhibited by the presence of a substance containing the sulphydryl group. It is suggested that the toxic action of the arsenic compound depends on a condensation of the latter with the glutathione of the organisms and a consequent derangement of their cell respiration. The variations in arsenic resistance of different strains are thus explained as being due to the different amounts of glutathione which may be present in the organisms in excess of their normal physiological requirements. C. R. H.

Comparative Studies on Narcosis with Chloroform and Dichloroethylene. Effect on Protein Balance of Rats. R. W. RIGLER and R. RINGEL (*Z. ges. exp. Med.*, 1923, **37**, 429—441; from *Chem. Zentr.*, 1924, i, 686).—Chloroform produces a marked decrease of respiration frequency, an effect which is not observed with *cis*-dichloroethylene. There is a pronounced rise in the curve for urine nitrogen where chloroform is administered. Both *cis*- and *trans*-dichloroethylene are without serious effect on the nitrogen balance. G. W. R.

Properties of the Constituents of Witte's Peptone. J. J. ABEL and E. M. K. GEILING (*J. Pharm. exp. Ther.*, 1924, **23**, 1—27).—By half-saturation and subsequent complete saturation with ammonium sulphate of a solution of Witte's peptone, there were obtained two albumose fractions. From the filtrate a further fraction soluble in acid alcohol was obtained. The albumose fractions were only slightly toxic, but the alcohol-soluble fraction behaved physiologically like histamine. Further, this fraction gave the Pauly reaction. The authors consider that the toxic substance is histamine, but that its origin is not bacterial. C. R. H.

Active Principles of Peptone. A. J. CLARK (*J. Pharm. exp. Ther.*, 1924, **23**, 45—54).—Peptones contain a substance, soluble in alcohol, having a physiological action resembling that of extracts of the posterior lobe of the pituitary; there is sometimes also found a second alcohol-soluble substance with sympathomimetic properties. No evidence could be found of the presence of histamine. The author considers that the lethal action of peptone injected intravenously is due to the alcohol-insoluble portion, although this portion is without action on isolated organs. C. R. H.

New Synthetic Nitrophenol Glucosides and the Disinfectant Action and Toxicity of the Nitrophenols. E. GLASER and W. WULWEK (*Biochem. Z.*, 1924, **145**, 514—534).—o-*Nitrophenol tetra-acetyl glucoside*, $C_6H_4O_2N{\cdot}O{\cdot}C_6H_7O_5(Ac)_4$, long, colourless needles, m. p. 158—159°, $[\alpha]_D^{18}$ +36·14°, is obtained by the action of an aqueous alkaline solution of nitrophenol on tetra-acetylbromoglucose in acetone, and on hydrolysis with ammonia in methyl alcohol it yields β-o-*nitrophenol glucoside*, $C_6H_4O_2N{\cdot}O{\cdot}C_6H_{11}O_5,H_2O$, colourless, hygroscopic crystals, m. p. 130—131°, having $[\alpha]_D^{14}$ −82·72°. m-*Nitrophenol tetra-acetyl glucoside*, m. p. 136—137°, $[\alpha]_D^{18}$ −18·26°, β-m-*nitrophenol glucoside* (+1H_2O), m. p. 167—168°, $[\alpha]_D^{22}$ −84·89°, p-*nitrophenol tetra-acetyl glucoside*, m. p. 174—175°, $[\alpha]_D^{18}$ −27·17°, and β-p-*nitrophenol glucoside* (+1H_2O), m. p. 164—165°, $[\alpha]_D^{22}$ −99°, are obtained in analogous manners. The three glucosides are hydrolysed by emulsin. The nitrophenols are intermediate in bactericidal power between phenol and the cresols, the meta compound being the most active, whilst the corresponding glucosides formed from them are devoid of disinfectant properties. The para compound is the most toxic of the three nitrophenols,

whilst the derived glucosides have but a slight toxicity. This is correlated with the detoxication of phenols by conjugation with glucuronic acid in the animal organism. J. P.

Quantitative Protozoöcidal Comparison of some Opium Alkaloids. C. E. Bills and D. I. Macht (*J. Pharm. Exp. Ther.*, 1924, **23**, 261—268).—Adopting unity as representing the toxicity of morphine to *Paramœcium* at p_H 5·7, the degree of toxicity of various opium alkaloids is as follows: morphine 1, codeine 1, dionine 2, heroine 7, thebaine 30, pantopium (the total alkaloids of opium) 30, papaverine 30, peronine (benzylmorphine) 100. With increasing p_H (6·6—7·7), morphine becomes less toxic, whilst codeine, heroine, and thebaine become much more toxic. Some evidence exists in favour of the view that *Paramœcia* become more resistant to given opium alkaloids after being subjected to non-lethal doses of the same alkaloid. J. P.

Behaviour of Bacteria towards the Alkaloids. H. H. Green and I. Lonstein (*J. S. Afr. Chem. Inst.*, 1924, **7**, 6—8).—The authors have isolated a non-spore-forming aërobe from nicotine sheep-dips; the organism does not liquefy gelatin, does not form acid or gas from dextrose, lactose, sucrose, or glycerol, is non-chromogenic, and non-diastatic. It destroys nicotine rapidly when the latter is the sole source of food supply as regards nitrogen and carbon, but if grown in media containing ammonium salts or simple nitrogenous compounds the organism loses its power of destroying nicotine. The organism tolerates morphine and atropine in concentrations up to 2%, but its growth is inhibited by strychnine, brucine, and quinine. Numerous putrefying organisms will grow in media containing 0·2% of nicotine, morphine, or atropine but not in those containing strychnine, brucine, or quinine. W. P. S.

Diastases. The Two Enzyme Theory. K. Hizume (*Biochem. Z.*, 1924, **146**, 52—71).—The liquefying action of human salivary diastase is increased in the same way as the saccharifying power by potassium and sodium chlorides and bromides, whilst iodides and fluorides are devoid of action. Diluted blood-serum has a similar activating effect. Dialysis lowers the liquefying power of saliva on starch, and this is entirely regenerated by the addition of chlorides and bromides. Nitrates act in a similar way on dialysed and undialysed saliva, nitrites are less active, whilst sulphates have no action on undialysed, but regenerate the activity of dialysed saliva. Alkalis and acids exert the same influence on the liquefying properties as on the saccharifying action of salivary diastase. The liquefying and saccharifying powers of malt diastase are not affected by salts. Maltose and dextrose protect salivary diastase from inactivation by heat, whilst sucrose and lævulose are much less active in this respect. Chlorides, bromides, and diluted serum also protect the enzyme against heat-inactivation, whilst iodides and nitrates have no such action. Malt diastase is more easily inactivated by heat in the presence of chlorides and bromides than in their absence (cf. A., 1923, i, 1254). J. P.

Purification of Malt Diastase by Electro-dialysis and Electro-osmosis. II. R. FRICKE (*Ber.*, 1924, **57**, [*B*], 765—768).—Improved methods are described for the preparation of the membranes and anode and for the regulation of the acidity of the solutions in the purification of malt diastase by electro-dialysis (cf. Fricke and Kaja, this vol., i, 469). The activity of the ultimate products is not thereby increased, but the heavy incidental losses of material are avoided. Increased attention to the acidity of the solutions in the electro-osmotic experiments has resulted in improved activity in the malt diastase, which, however, is very unstable in solution. H. W.

Influence of the New Sulphur-containing Amino-acid (Mueller) on the Activity of Pancreatic Amylase. M. L. CALDWELL (*J. Biol. Chem.*, 1924, **59**, 661—665).—The new amino-acid (cf. A., 1923, i, 869; this vol., i, 438) exerts a favourable influence on the amylolytic action of pancreatic amylase which is similar to that previously observed with naturally occurring α-amino-acids. C. R. H.

Liver Amylase. O. HOLMBERGH (*Z. physiol. Chem.*, 1924, **134**, 68—96).—The value of $Sf=K\times$(g. maltose formed from starch)/(g. preparation used), K being the unimolecular reaction constant, differs for samples from various lobes of a pig's liver, the mean value being 0·0038. In all cases, it is very much less than the value obtained for a piece of pancreas. The addition of liver substance to a pancreas extract results in an activity lower than the sum of the activities of the two components. It appears that the liver contains a substance which inhibits pancreatic amylase. The activity of liver amylase is highest at p_H 6·9, and in presence of 0·008—0·5N-sodium chloride or potassium chloride, or 0·008—0·04N-calcium chloride. Sodium iodide decreases the production of maltose, but increases that of dextrose. Various methods of extracting liver amylase have been investigated. Dialysis at first increases the activity of the preparation, Sf increasing more than 500%, but further dialysis results in a decrease of activity. The action of liver amylase on starch is inhibited by maltose, but this inhibition disappears if the maltose is removed by maltase. If yeast is treated with toluene containing ethyl acetate so as to destroy the maltase, it no longer retains its power of increasing the activity of amylase. W. O. K.

Invertase. IV. H. VON EULER and K. JOSEPHSON (*Ber.*, 1924, **57**, [*B*], 859—865; cf. A., 1923, i, 721; this vol., i, 466).—Elementary analyses of purified invertase (*If* 225—245) gave results which are closely similar to those of the proteins, the slight discrepancies being probably attributable to the presence of carbohydrates in invertase. Colorimetric determinations indicate the presence of tryptophan 5·5% and histidine $<6\%>2\%$ in invertase; tyrosine is absent. As judged from the sulphur content, cystine is present to the extent of 2%. H. W.

Uniformity in Invertase Action. III. Stability of the Enzyme. J. M. NELSON and R. W. E. KERR (*J. Biol. Chem.*, 1924, **59**, 495—527).—Invertase preparations could be made abnormal by treatment with dialysed iron, accompanied by an increase in the activity per unit of dry weight. Abnormal invertase prepared in this way is unstable at p_H about 4·5 and 25°. It can be re-stabilised by the addition of inactivated normal invertase preparation. This re-stabilisation may be effected in varying degree according to the concentration of the added inactivated normal invertase preparation, and is reversible with dilution. Normal invertase preparation which is rendered unstable by dilution is re-stabilised by the addition of gelatin, egg-albumin, or inactivated normal invertase preparation. At p_H 2·2 and 25°, abnormal invertase is less stable than normal invertase, and the addition of inactivated normal invertase preparation causes an increase in the stability of the former and a decrease in that of the latter. The rate of inactivation of invertase solutions at p_H 2·2 and 25° is higher in the more concentrated solutions and falls off in the latter part of the inactivation. The inactivation of concentrated invertase solutions brought about in this manner is partly reversible with dilution and changing the p_H from 2·2 to about 4·5, although the reversibility is not observed with less concentrated solutions. At p_H 4·8 and 60—65°, both the normal and the abnormal invertase preparations possess the same stability. D. R. N.

Characteristics of Invertase Action. J. M. NELSON and G. BLOOMFIELD (*J. Amer. Chem. Soc.*, 1924, **46**, 1025—1043).—Arising out of the observation that different invertase preparations at different temperatures gave a maximum velocity of inversion at nearly the same sucrose concentrations (Nelson and Vosburgh, A., 1917, ii, 252), the influence of the temperature and of the hydrogen-ion concentration on the relation between the sucrose concentration and the rate of hydrolysis has been studied. The sucrose concentration at which the hydrolysis reaches its maximum velocity is independent of the temperature and hydrogen-ion concentration. Further, the limits of hydrogen-ion concentration within which the hydrolysis with invertase follows a normal course extend from p_H 2·75—3·3 (depending on the temperature) in the acid region to p_H 8·4 in the more alkaline region. Between 25° and 35°, the hydrogen-ion concentration at which invertase first shows inactivation decreases regularly. The zone of the optimum action of invertase at 25°, 30°, 35° lies between the hydrogen-ion concentrations p_H 4·5 and 5·0, which are narrower limits than previously determined. The relation between the activity (n) and the hydrogen-ion concentration approximately satisfies the equation for the dissociation residue curve, $\rho=[H^{\cdot}]/([H^{\cdot}]+k)$, where ρ is the fraction of the compound not dissociated and k is the dissociation constant, as claimed by Michaelis and Davidsohn (A., 1911, i, 1052). The temperature does not affect this relation. The temperature coefficient of the hydrolysis of sucrose in the presence of invertase increases with decreasing acidity,

hence the hydrolysis is inherently different from that by acid, where the same coefficient is independent of the hydrogen-ion concentration. The hydrolysis of sucrose is thus shown to involve two distinct stages, one of which is characterised by the sucrose concentration at which the hydrolysis reaches its maximum velocity and is independent of the temperature and acidity, whilst in the other it changes with each of these. A. C.

Calculation of the Activity–p_H Curve of Invertase. H. von Euler, K. Josephson, and K. Myrbäck (*Z. physiol. Chem.*, 1924, **134**, 39—49).—Assuming that the adsorption compound between invertase and sucrose dissociates as a weak acid between p_H 5 and p_H 8 and that the undissociated compound only is active, the variation of the rate of inversion with the p_H can be calculated. The experimental results agree well with theory. If, as has been shown to be probable by Willstätter and Kuhn (cf. A., 1923, i, 401), raffinase is identical with invertase, and this enzyme has an affinity constant for raffinose of only about 1/15 of that for invertase, then it may be shown by calculation that the variation with p_H of the rates of fermentation of the two sugars should be very similar, as is found experimentally. W. O. K.

Affinity of Invertase for Different Sugars. II. K. Josephson (*Z. physiol. Chem.*, 1924, **134**, 50—67).—Invertase suffers no loss of activity when it is kept for 30 minutes at p_H 2·63. There is thus no destruction of invertase due to acid alone. The depressing effect of acid on the activity of invertase which appears when the inversion is carried out in a medium more acid than p_H 4·5 (the optimum p_H) is shown to be largely accounted for by the change in the affinity constant K_M of the enzyme for the substrate occasioned by the low p_H. A small discrepancy between the theoretical and experimental results is probably caused by the basic dissociation of the enzyme–substrate compound. Inversion is inhibited by dextrose and lævulose less at p_H 2·75 than at p_H 4·5. In the case of dextrose, the inhibition is maximum at p_H 4·5, whilst in the case of lævulose, inhibition continues to increase with the p_H. W. O. K.

Hydrolysis of the Endosperm of *Phytelephas macrocarpa* by its own Enzymes. F. J. Paton, D. R. Nanji, and A. R. Ling (*Biochem. J.*, 1924, **18**, 451—454).—Vegetable ivory shavings contain an enzyme which hydrolyses the mannan present in them to mannose and a trisaccharide which is presumably mannotriose. The hydrolysis was greatest at about p_H 4·2. When the enzyme is allowed to act for a long period, namely, 10 days, mannose alone is produced. It is probable, therefore, that the trisaccharide is an intermediate product. S. S. Z.

Synthesising Action of α-*d*-Mannosidase in Presence of Ordinary Glycol and Glycerol. H. Hérissey and J. Cheymol (*Compt. rend.*, 1924, **178**, 1372—1374).—Combination of mannose with glycol or glycerol is effected by the action of the α-*d*-mannosidase contained in germinated lucerne seeds (cf. this vol., i, 234). T. H. P.

Enzymic Hydrolysis of Hexose-monophosphoric Acid by Extracts of the Femur. Y. TAKAHASHI (*Biochem. Z.*, 1924, **146**, 161—163).—The hexose-monophosphate prepared by Neuberg (A., 1918, i, 423) by partial hydrolysis of hexose-diphosphate, is hydrolysed by aqueous extracts of the femur with the liberation of phosphoric acid (cf. Robison, A., 1922, i, 730). J. P.

Dried Yeast. H. SOBOTKA (*Z. physiol. Chem.*, 1924, **134**, 1—21).—The rate of fermentation of dextrose by yeast dried by various methods has been measured by determining the rate of production of carbon dioxide. With such dried yeasts there usually occurs a more or less marked period of induction. Increase of the concentration of the yeast decreases this period. If the yeast is first of all incubated with sugar solution the incubation period disappears. After being ground up in a mortar, dried yeast ferments sugar more slowly. Determination of the sugar at intervals during the fermentation by dried yeast shows that a certain disappearance of the carbohydrate takes place, amounting to from 20—50% of the sugar used, which cannot be accounted for by the carbon dioxide produced. W. O. K.

Mechanism of Alcoholic Fermentation. III. A. LEBEDEV (*Z. physiol. Chem.*, 1924, **134**, 160; cf. this vol., i, 464).—The liquid obtained after fermentation of sugar in presence of phosphate, on treatment with lead acetate and hydrogen sulphide, yielded no osazone but a white precipitate of either hydrazone or hydrazide. W. O. K.

Adenine Hexoside from Yeast. P. A. LEVENE (*J. Biol. Chem.*, 1924, **59**, 465—472).—The sugar constituent in adenine hexoside from yeast (A., 1912, i, 320) appears to possess certain peculiarities and differs from other known hexoses. It is not oxidised by bromine water and hence is ketonic, although apparently it is not a common β-ketohexose (A., 1915, ii, 494). The mutarotation of the phenylosazone of the new sugar closely resembles that of *d*-gulosazone, the initial rotation being practically 0° and the equilibrium slightly to the right. The m. p. of the new osazone is 165° (corr.), which is nearly the same as that of gulosazone, although the decomposition points are 208° and 180°, respectively. It further differs from gulosazone in being less soluble in alcohol and in water. These differences are more marked in the two *p*-bromophenylosazones. Taking dextrose as a standard of reduction, 1 g. of the hexoside should yield 0·6 g. of the sugar, whereas the maximum yield obtained from the hexoside was only 0·18 g. Further, on the basis of the rotation of the osazones, the sugar should belong to *d*-series, but *d*-sorbose rotates to the left, whereas the new sugar is dextrorotatory. Thus the new sugar does not seem to be identical with any one of the known β-ketohexoses. D. R. N.

Effect of Nitrogenous Nutrition on the Activity of Brewer's Yeast. I. BAY (*Compt. rend. Soc. Biol.*, 1923, **89**, 1044—1045; from *Chem. Zentr.*, 1924, i, 680).—Fermentation with brewer's

yeast is most active and produces the maximum amount of ethyl alcohol and acid at 15° in a bouillon containing 0·1% of ammonium hydrogen carbonate. G. W. R.

Variability of Lactic Acid Fermentation. A. LUMIÈRE (*Ann. Inst. Pasteur*, 1924, **38**, 344—357; cf. this vol., i, 353).—The author replies to criticisms of his previous work on the subject, and brings forward further experimental evidence in support of his contention that, provided his technique is rigidly followed, lactic acid fermentation is a perfectly regular process, both in normal media and in the presence of small concentrations of antiseptics, and, in the latter case, regardless of whether or not the bacteria used are acclimatised to the antiseptic. C. R. H.

Fermentation of the Unsaturated Dicarboxylic Acids. I. Fumaric Acid. J. H. QUASTEL (*Biochem. J.*, 1924, **18**, 365—380).—Succinic and fumaric acids are fermented by *Bacillus pyocyaneus*, with the production of lower fatty acids. In the case of fumaric acid, acetic acid is chiefly formed. This fermentation is accelerated by aëration, and proceeds more rapidly in the case of fumaric acid than in that of succinic acid. A 1% solution of ammonium fumarate is entirely utilised in 30 hours. The fermented fumarate medium gives colour tests with nitroprusside and with guaiacol due to the formation of pyruvic acid. The colour tests can be utilised as a test for differentiating *B. pyocyaneus* and *B. fluorescens liq.* from other bacteria capable of growing on a fumarate medium and which do not give these colour reactions. From the quantities of oxygen utilised and carbon dioxide formed during the fermentation of a known amount of fumaric acid a scheme representing the intermediate stages of fermentation in which oxalacetic acid figures is advanced; 90% of fumaric acid can be accounted for in the fermentation. S. S. Z.

Optimum and Limiting Concentrations of Hydrogen Ions for Bacterial Cultures. Tendency of Cultures to Approach the Optimum Concentrations. CLUZET, ROCHAIX, and KOFMAN (*Compt. rend.*, 1924, **178**, 1638—1639).—Cultures of *Bacillus coli*, *B. paratyphosus* B, and of Ebert's and Flexner's bacilli exhibited optimum and lower and upper limiting concentrations of hydrogen ions, these being different for the different organisms. During normal bacterial growth, the cultures tended to become gradually more alkaline but not to overstep the optimum hydrogen-ion concentration. If development is restricted owing to excessive acidity or alkalinity, the bacteria appear to exert an alkaligenic or acidogenic function, the reaction becoming progressively displaced towards the optimum value. T. H. P.

Effect of Iron and Zinc on the Development of *Aspergillus niger* in the Presence of Dextrose. A. FROUIN (*Compt. rend. Soc. Biol.*, 1923, **89**, 986—988; from *Chem. Zentr.*, 1924, i, 679).—The favourable effect of zinc and ferrous iron on the growth of *Aspergillus* in the presence of sucrose cannot be attributed to the

presence of dextrose. Ferrous iron is unfavourable to the formation of dry mycelial tissue, but favourable to spore formation. G. W. R.

Transformation of Quinic Acid by Moulds. W. Butkewitsch (*Biochem. Z.*, 1924, **145**, 442—460).—The coloration observed to develop in cultures of *Citromyces* and *Penicillium* containing sodium quinate (A., 1922, i, 707) is ascribed to the formation of condensation products (with iron) by phenolic compounds into which quinic acid is transformed by the moulds. Protocatechuic acid is the most important of these phenols, but pyrocatechol, quinol, and quinone are supposed also to be formed. The subsequent disappearance of the coloration in old cultures is ascribed to the decomposition of the condensation products with formation of oxalic acid, which is later oxidised to carbon dioxide. Only those moulds which can bring about the formation of the intermediate phenolic compounds from quinic acid are able to utilise it as a source of carbon, and both processes are influenced in the same way when zinc sulphate is added to the culture. Moulds capable of forming phenolic compounds from quinic acid also ferment sugar with formation of citric acid, and a possible correlation of the two processes is suggested. These results are regarded as opposing the view of Kostytschev (A., 1921, i, 83) that quinic acid is first transformed by moulds into sugar.

J. P.

Comparison of Yields from the Point of View of Energy in the Development of Moulds utilising Carbohydrates or Proteins, and Specific Dynamic Action. E. F. Terroine, R. Bonnet, R. Jacquot, and G. Vincent (*Compt. rend.*, 1924, **178**, 869—872).—*Aspergillus niger* and *A. oryzæ* were cultivated in solutions of glucose to which ammonium sulphate had been added, of silk peptone, and of gelatin, the growths being analysed from the thermal point of view. The results, together with those obtained in the course of other investigations (Terroine, Bonnet, and Joessel, *Compt. rend.*, 1923, **177**, 900), lead to the generalisation that in living organisms formation of one carbohydrate from another involves extremely small energy loss, which is increased when carbohydrate is formed from fat and considerably so if from proteins. The energy utilisation coefficients of carbohydrates and proteins are in the ratio of about 100 to 140. H. J. E.

Metabolism of Acid-fast Bacteria. I. H. Braun, A. Stamatelakis, and S. Kondo (*Biochem. Z.*, 1924, **145**, 381—397).—An investigation of the growth of the acid-fast Timothy bacillus, various strains of butyric bacillus, urine and Trumpet bacilli in nutrient media containing various sources of carbon (organic acids, alcohols, and carbohydrates), nitrogen (amino-acids, urea, and uric acid), and inorganic salts. J. P.

Susceptibility of Lipases of Various Origin to Toxins. P. Rona and H. Petow (*Biochem. Z.*, 1924, **146**, 144—152).—The susceptibility to toxic inactivation (A., 1923, i, 1258) shown by purified pancreatic, liver, and serum lipases is of the same order

as that of the crude aqueous extracts containing these enzymes. The specific reactions of the lipases to quinine and atoxyl are preserved in artificial mixtures of the enzymes, serum lipase being inactivated by quinine, and serum and liver lipases by atoxyl. J. P.

Kinetics of Trypsin Digestion. II. Conditions Under Which the Reaction is Unimolecular. J. H. NORTHROP (*J. Gen. Physiol.*, 1924, **6**, 417—428).—If certain conditions are observed, the hydrolysis of casein by trypsin is accurately represented by the unimolecular formula $dx/dt=KE(A-x)$, where K is a constant, E is the quantity of enzyme used, A is the original concentration of casein, and x the concentration of casein at the time t. The conditions are that the temperature is low, to prevent inactivation of the trypsin, that much trypsin is used so that inhibition by the products of the reaction is negligible, and that the course of the reaction is followed by determining the actual amount of casein present at various times so that the effect of consecutive reactions is eliminated. Under these conditions also, the effect of variations in the initial concentration of the trypsin is predicted by the formula, but with increasing casein concentrations the value of K decreases and ultimately becomes nearly inversely proportional to the casein concentration. It is suggested that this is due to the existence of an equilibrium between casein and water in which casein can be replaced by the first cleavage products, since, if casein is dissolved in a freshly-prepared solution of digested casein, the reaction is typically unimolecular in every respect. W. O. K.

Kinetics of Trypsin Digestion. III. The Course of the Reaction with Constant Substrate under Conditions causing Inactivation of the Enzyme. J. H. NORTHROP (*J. Gen. Physiol.*, 1924, **6**, 429—437).—When gelatin is hydrolysed in concentrated solution by a large amount of trypsin at 60° and at p_H 6·0, inactivation of the trypsin takes place, and so the reaction is apparently not unimolecular. If, however, determination is made by the method of Northrop and Hussey (A., 1923, ii, 271) of the trypsin present at various times during the course of the reaction, it appears, from theory and experiment, under these conditions, (*a*) that the rate of reaction is proportional to the concentration of trypsin present at the time, (*b*) that the reaction is approximately unimolecular if the total hydrolysis observed is taken as the amount of substrate available, (*c*) that the velocity constant calculated in this way should agree with the constant for the decomposition of the enzyme, and that it should be independent of the concentration of the enzyme instead of proportional to it, and (*d*) that the total amount of substrate decomposed should be proportional to the amount of trypsin added at the beginning instead of independent of it. W. O. K.

Kinetics of Trypsin Digestion. IV. The Course of the Reaction when both Substrate and Enzyme Concentrations are Decreasing. J. H. NORTHROP (*J. Gen. Physiol.*, 1924, **6**, 439—452).—When edestin is hydrolysed by trypsin at p_H 7·0 at

40° in the presence of a high concentration of sodium chloride which decreases the activity of the trypsin and increases the solubility of the edestin, rapid inactivation of the trypsin occurs, and the reaction follows the equation $K=[\log(A_1/A_2)]/(T_1-T_2)E_t$, where A_1 and A_2 are the concentrations of the edestin at times T_1 and T_2 respectively and E_t is the concentration of the enzyme during the interval T_1-T_2. If it is assumed that the activity of the enzyme decreases unimolecularly, the theoretical results are obtained when high enzyme and low edestin concentrations are used. With low enzyme and high edestin concentrations, the effects of the products on the reaction become too large to be negligible. W. O. K.

Action of Chymosin on the Proteins of Milk. I. Action of Chymosin on Colostrum. J. ZAYKOWSKY (*Biochem. Z.*, 1924, **146**, 189—197).—From a comparison of the coagulating action of chymosin (rennin) on colostrum and on milk at varying acid concentrations, support is gained for the view that rennin and pepsin are not identical. J. P.

Detection of Ferment Processes Conditioned by Immunisation. I. E. KUPELWIESER (*Biochem. Z.*, 1924, **145**, 492—504).—Using the refractometric method described by Pregl and de Crinis (*Fermentforschung*, 1917, **2**, 58) and in contrast to the findings of these authors, no proteolytic action of serum on placenta proteins could be demonstrated in cases of pregnancy. J. P.

Detection of Ferment Processes Conditioned by Immunisation. II. E. KUPELWIESER and H. WASTL (*Biochem. Z.*, 1924, **145**, 505—513).—The sera of guinea pigs immunised with inactivated ox-serum have no proteolytic action on the antigen (cf. Pfeiffer and Mita, *Z. Immunitätsforsch.*, 1910, **6**, 18; Abderhalden and Pinkussohn, *Z. physiol. Chem.*, 1910, **64**, 100). J. P.

Proteinogenous Amines. XVII. Faculty of Normal Intestinal Bacteria to form Toxic Amines. XVIII. Production of Histamine, Tyramine, and Phenol in Laboratory Media by Intestinal Organisms. XIX. Factors involved in the Production of Phenol by the Colon Group. XX. Presence of Histamine in the Mammalian Organism. M. T. HANKE and K. K. KOESSLER (*J. Biol. Chem.*, 1924, **59**, 835—853, 855—866, 867—877, 879—888. **XXI. Intestinal Absorption and Detoxication of Histamine in the Mammalian Organism.** K. K. KOESSLER and M. T. HANKE (*ibid.*, 1924, **59**, 889—903).—XVII.—The action was observed of the mixture of bacteria in human fæces on histidine and tyrosine in a synthetic medium composed of salts and glycerol. Out of a series of twenty-six cases, it was found that 62% decarboxylated histidine, 65% decarboxylated tyrosine, and 46% could do both. Phenol was never produced from tyrosine; in three cases small amounts of *p*-hydroxyphenyl-lactic acid were obtained. During the bacterial

action the hydrogen-ion concentration of the fluid uniformly increased.

XVIII.—The decarboxylating action on histidine and tyrosine of two strains of colon bacilli was studied in milk, blood broth, and ascitic fluid broth. Amines were only produced in media containing carbohydrate and in which an acid reaction was developed. The organism which produced tyramine in an acid medium produced phenol in an alkaline one.

XIX.—An extension of the preceding paper emphasising the authors' view that amine production is a protective mechanism of the bacteria against a rise in hydrogen-ion concentration of the medium.

XX.—Details are given of a method for the colorimetric determination of histamine in mixtures such as intestinal contents. In human fæces, there were found 6—20 mg. of histamine in 500 g. of material, and amounts of the same order of magnitude in cæcal contents. No evidence was found of the presence of histamine in the human liver, but it was demonstrated in the liver of the dog.

XXI.—A physiological study was made of the systemic effects observed after the introduction of histamine into different parts of the alimentary canal. A comparison of the rate of absorption, as measured by the disappearance of the substance from the alimentary canal, with the mildness of the resulting systemic effects, leads the authors to conclude that histamine may be detoxicated during its passage through the intestinal wall. C. R. H.

Culture of Moulds on Amino-acids and Mechanism of the Specific Dynamic Action. E. F. Terroine, S. Trautmann, R. Bonnet, and R. Jacquot (*Compt. rend.*, 1924, **178**, 1488—1490). —By growing *Aspergillus niger* and *A. oryzæ* on media containing glycocoll, alanine, valine, leucine, or glucosamine, it is shown that the energy liberated is constant and independent of the nature of the amino compound or organism. The energy change must therefore be associated solely with de-aminisation. A. B. H.

Production of Carbamide during Ammonification by the *Microsiphoneæ*. G. Guittonneau (*Compt. rend.*, 1924, **178**, 1383—1385).—When grown in an inorganic solution to which peptone was added as sole organic nutriment, certain of the *Microsiphoneæ* produced carbamide in considerable proportions and at the same time ammonium salts neutral to phenolphthalein accumulated in the liquid. The carbamide may be formed as a waste product or may be an intermediate compound in the assimilation of the hydrolytic products of the peptides. As regards its practical significance, carbamide readily enters the general cycle of vegetation owing to its transformation in the soil into ammonium carbonate, and, moreover, most plants secrete urease.

On the other hand, such liberation of carbamide results in loss of gaseous nitrogen if it is produced in contact with the nitrous acid displaced from nitrites by the acid formed in the various

fermentations of carbonaceous material. These phenomena may occur in the soil and also help to explain the enormous losses of nitrogen taking place during the purification of sewage. T. H. P.

Occurrence of Peroxide in Cultures of *Pneumococcus*. O. T. AVERY and H. J. MORGAN (*J. Exp. Med.*, 1924, **39**, 275—287). —Peroxide formation was observed with various strains of *Pneumococcus*, *Staphylococcus hæmolyticus*, and *S. mucosus*, but not with *S. aureus*. With the first-named, there must be free access of air, and absence of catalase, peroxydase, etc.; the product is unstable, and conditions leading to its disappearance are mentioned.

CHEMICAL ABSTRACTS.

Participation of a Peroxydase in the Appearance of Pigment in *Drosophila melanogaster* (Lœw.). DE LUNA (*Compt. rend.*, 1924, **178**, 878—881; cf. this vol., i, 348).—Both an oxydase and a peroxydase play a part in the pigmentation of *Drosophila*; the former is probably tyrosinase, and the distribution of these enzymes is similar to that of the pigment. Rate of pigmentation is a function of temperature, but anæsthetics retard the fixation of oxygen on the colourless matter (A., 1904, ii, 831).

H. J. E.

Influence of *X*-Rays on the Catalase of Liver. A. MAUBERT, L. JALOUSTRE, P. LEMAY, and C. GUILBERT (*Compt. rend.*, 1924, **178**, 889—891; cf. Maubert, Jaloustre, and Lemay, A., 1923, i, 723).—The effect of *X*-rays is to decrease the activity of liver catalase in proportion to the duration of exposure and the intensity of radiation. Detailed results are given, but comparison is difficult as the catalase preparations used were not identical in each case.

H. J. E.

Sorptive Power of Metallic Hydroxides [for Invertase]. II. H. VON EULER and R. NILSSON (*Z. physiol. Chem.*, 1924, **134**, 22—38).—Freshly precipitated lanthanum hydroxide adsorbs invertase even more completely than does aluminium hydroxide. It adsorbs more at p_H 8·1 than at p_H 5·6. Its power of adsorption decreases on keeping. The invertase adsorbed by lanthanun hydroxide is not adsorbed irreversibly unless the hydroxide is precipitated in presence of the enzyme, when some inactivation takes place.

W. O. K.

Coagulation and Vegetable Life. J. AMAR (*Compt. rend.*, 1924, **178**, 1317—1319; cf. this vol., i, 687; ii, 144).—Experiments on starch, on beans, and on the leaves of the spindle tree are described, the results indicating the marked de-coagulating effects produced by sodium chloride and other sodium salts and hence the importance of such salts in promoting osmotic interchanges and the general health of the vegetable organism.

T. H. P.

Production of Ozone by Green Plants. H. COUPIN (*Compt. rend.*, 1924, **178**, 1572—1573).—Some evidence has been obtained

that small quantities of ozone are given off, together with oxygen, from green plants when placed in a damp chamber in the light for 24 or 48 hours. Since in the dark, or with plants devoid of chlorophyll, no ozone is produced, it is concluded that ozone production is probably connected with carbon dioxide assimilation. J. W. B.

Equilibrium of the Cellular Constituents and Intensity of the Oxidations of the Cell. Imbibition and Oxidation. Case of Reviviscent Plants. A. MAYER and L. PLANTEFOL (*Compt. rend.*, 1924, **178**, 1385—1388).—The authors have investigated the proportions of carbon dioxide formed when *Hypnum triquetrum*, soaked in water to bring it to a reproducible degree of imbibition and then allowed to dry to different extents, is kept in an enclosed space in the dark at 20°. The respiratory intensity either passes through a maximum at 50—60% of water in the moss, or gradually increases to a constant, or passes through a maximum at about 40% of water, according as it is referred to 1 g. of the wet moss, or to 1 g. of the dry matter, or to 1 g. of the water present. It is concluded that, other things being equal, there are definite proportions of water and of the other constituents of the cell for which the cellular oxidations exhibit a maximum intensity. T. H. P.

"Auximones," and the Growth of the Green Plant. N. A. CLARK and E. M. ROLLER (*Soil Sci.*, 1924, **17**, 193—198).—*Lemna major* was grown in a series of artificial culture solutions and compared with that grown in soil suspensions. Healthy growth and reproduction depended on a requisite proportionality of dissolved salts. Neither "auximones" (Bottomley) nor organic matter were essential. In the absence of these latter, during 4 months closely followed the equation: $\log_{10}N/N_0=k(t-t_0)$, where N=number of plants present and t=time. A. G. P.

Effect of General Anæsthetics on the Respiration of Cereals. I. Carbon Dioxide Production. E. P. SMITH (*Ann. Bot.*, 1924, **38**, 261—272).—Chloroform, ether, and ethyl alcohol in varied concentrations have similar effects on the carbon dioxide output from seedlings of wheat, rice, and oats; the first effect is a decrease in the rate of respiration, followed by an increase to a maximum and a final depression. With chloroform, recovery is possible only after very short exposures, whether continuous or intermittent; with ether recovery can take place even after 6 hours' exposure, provided the respiration does not fall below 60%. Experiments with the corolla of *Ipomœa* indicate that the effect of the anæsthetic on the permeability to carbon dioxide of the plasma membrane must also be taken into account, and that the apparent maximum respiration after treatment with an anæsthetic may be due to a release of carbon dioxide retained during a period of decreased permeability. E. M. C.

Anaërobic Experiments with Argon. W. A. CANNON and E. E. FREE (*Carnegie Inst. Yearbook*, 1921, **20**, 63).—Experiments with roots and other parts of plants under partial anaërobic conditions show that the amount of oxygen necessary for growth is

the same when nitrogen or argon is used as the diluent gas, but less in the case of helium and hydrogen. The difference is probably concerned with the relative rates of diffusion of oxygen through the gases. A. A. E.

Carbohydrate–Amino-acid Relation in the Respiration of Leaves. H. A. SPOEHR and J. M. MCGEE (*Carnegie Inst. Yearbook*, 1921, **20**, 60—61).—Carbon dioxide evolved in respiration was determined by a conductivity method. The stimulating effect of amino-acids (glycine, alanine, and asparagine) is most marked with dextrose as the carbohydrate food, noticeable with sucrose but not with mannose, and depressed by lævulose. No explanation is advanced. A. A. E.

The First Carbohydrates that Originate during the Assimilatory Process. Physiological Study with Variegated Leaves. T. WEEVERS (*Proc. K. Akad. Wetensch.*, 1924, **27**, 46—56).—In ten out of twelve different plants examined, the variegated parts of the leaves contain only sucrose, and the green parts both sucrose and monoses. The presence of monoses in the assimilating leaf-parts and their absence from the non-assimilating full-grown variegated leaves support the view that, in these plants, starch arises from the monoses and that the latter are, in general, the first sugars to be synthesised during the process of carbon assimilation. Confirmation of this view is furnished by the absence of starch as reserve material from three of the species, namely, *Aspidistra*, *Chlorophytum*, and *Ophiopogon*, which contain starch only in the stomata of both the variegated and the green parts of the leaf.

Complete proof has been obtained by depleting the full-grown leaves of the variegated *Pelargonium* of their sugar and starch by keeping the plants in the dark for two or three days and then exposing them to sunlight. Under these conditions, the first sugars to be formed as assimilation takes place are monoses, sucrose and starch appearing only later. Conclusive evidence is not available concerning the character of the initial monose, but in *Pelargonium zonale* lævulose seems to preponderate.

The variegated parts of the plants which contain sucrose contain also invertase, the fact that inversion does not occur in the living tissues being probably due to difference in localisation of the sugar and enzyme in the cell. T. H. P.

Nitrogenous Metabolism of the Higher Plants. V. Diurnal Variations in the Protein Nitrogen of Runner Bean Leaves. A. C. CHIBNALL (*Biochem. J.*, 1924, **18**, 387—394).—There is a definite fall in the protein content of bean leaves at night, due to the breaking down of the cytoplasmic material. The nitrogenous products of this protein decomposition are translocated away from the leaf. S. S. Z.

Nitrogenous Metabolism of the Higher Plants. VI. Rôle of Asparagine in the Metabolism of the Mature Plant. A. C. CHIBNALL (*Biochem. J.*, 1924, **18**, 395—404).—The decomposition

products arising from protein metabolism in bean leaves consist in large part of asparagine and other unknown substances containing free amino-nitrogen. Asparagine seems to be the chief agent whereby nitrogen in a form suitable for re-synthesis of protein is conveyed from one part of the plant to another. S. S. Z.

Nitrogenous Metabolism of the Higher Plants. VII. Leaf Protein Metabolism in Normal and Abnormal Runner Bean Plants. A. C. CHIBNALL (*Biochem. J.*, 1924, **18**, 405—407).—The protein degradation products of two normal and two abnormal plants are given. S. S. Z.

Carbon Dioxide Production of Plant Roots as a Factor in the Feeding Power of Plants. F. W. PARKER (*Soil Sci.*, 1924, **17**, 229—247).—The carbon dioxide evolution of various plant roots differed considerably, but no relationship between this factor and the feeding power of the plant (as determined by plant composition) was found. The removal of carbon dioxide from media by aspiration had no effect on the composition of the plants. The amount of the various nutrient elements absorbed by plants per gram of carbon dioxide excreted by the roots differed with the plant type. A. G. P.

Variation of the Iodine in *Laminaria flexicaulis* at the Period of the Annual Shooting. P. FREUNDLER (*Compt. rend.*, 1924, **178**, 1625—1628; cf. this vol., i, 354).—The results of further analyses show that the variations in the iodine content of this alga are influenced by the principal factors which intervene in enzymic reactions. Such variations constitute one of the manifestations of the disturbance of the equilibria between the alga and the sea, and between the alga and the air, and appear to be due to temporary, progressive, and reversible modification in the state of combination of the iodine. T. H. P.

Extraction of Pectin from the Fruit Rind of the Lime (*Citrus medica acida*). F. HARDY (*Biochem. J.*, 1924, **18**, 283—290).—Under similar time conditions, the total quantity of pectinogen obtained by extraction from the dried white rind of lime fruits varies directly with the hydrogen-ion concentration of the extracting medium when carried out at temperatures below boiling point. The quantity also varies directly with the temperature if the final reaction of the extract is less acid than p_H 2·0. Alkaline extracts do not contain pectinogen. Autoclave treatment in acid medium hydrolyses the pectinogen. The viscosity of the extracts depends more on the conditions of extraction than on the pectinogen content. S. S. Z.

Pectins of *Apium graveolens*, of the Tubers of *Stachys tuberifera*, and of the Rind of *Citrus vulgaris*. Biochemical Method of Characterising Galactose applied to the Study of the Composition of these Pectins. J. CHARPENTIER (*Bull. Soc. Chim. biol.*, 1924, **6**, 142—156).—In the alcoholic extract of the

roots of *Apium graveolens* the presence of sucrose, mannitol, and a small quantity of a reducing sugar was demonstrated. The pectin of the same plant was obtained as a white powder, $[\alpha]_D$ +154·5°, which was coagulated in aqueous solution by the pectase of lucerne, by lead acetate, calcium and barium hydroxides, and by traces of hydrochloric acid. It yielded mucic acid when treated with nitric acid, and *d*-arabinose on hydrolysis with dilute sulphuric acid. The pectins of *Stachys tuberifera* and of *Citrus vulgaris*, with $[\alpha]_D$ +119·8° and +170·5°, respectively, also yielded mucic acid and arabinose and possessed properties similar to those of the pectin of *Apium*. From the hydrolysis product of the pectins of *Apium* and *Citrus*, treated with 70% aqueous ethyl alcohol in the presence of emulsin for 3 months, crystalline β-ethyl galactoside (m. p. 158—159°; $[\alpha]_D$ −5·3°) was isolated, yielding on hydrolysis dextrorotatory galactose and on oxidation mucic acid. It is concluded that the latter does not arise from galacturonic acid, and the presence of a galactan in these pectins is established. J. P.

Chemical Nature of the Cellulose Membrane. F. M. Wood (*Ann. Bot.*, 1924, **38**, 273—298).—The author has reinvestigated the methods of preparation and staining of plant-tissues in order to differentiate between cellulose and pectic compounds. The best conditions of preparation for double staining are those giving minimum oxidation and maximum hydration without disintegration. Tests for oxycellulose were made on a large number of stem and root sections both in the fresh state and after the use of many fixatives. Alcohol and glycerin should be avoided on account of their obstinate retention by cellulose and their liability to wash into the pectin and so disturb its reactions to dyes. Pectin is stained by hydrochlorides of amines, and cellulose by alkali salts of the disulphonic acids of compounds containing one or more azo groups. Methylene-blue is uncertain, owing probably to its containing sulphur. The membrane probably consists of cellulose, hydrocellulose, and oxycellulose in equilibrium, the two former generally predominating. E. M. C.

Nature and Amount of Substances Capable of Hydrolysis by Invertase and by Emulsin contained in Seeds of some *Leguminosæ*. H. Hérissey and R. Sibassié (*Compt. rend.*, 1924, **178**, 884—886).—Seeds of numerous species of *Leguminosæ* were examined. Reducing sugars were not detected and, if present, formed not more than 0·4% of the dry seeds. Aqueous extracts showed different degrees of dextrorotatory power, which was much diminished by the action of invertase; it is inferred that polysaccharides of strong dextrorotatory power are present. Stachyose was isolated from seeds of fenugreek, Provence lucerne, and *Indigofera*, and raffinose from those of *Anthyllis vulneraria* and Spanish sainfoin. Sucrose was present in the majority of the seeds, its presence in Constantinople acacia and in Indian liquorice (*Abrus abrus*) being demonstrated for the first time. Indications of glucosides were obtained with purple broom and *Copaifera officinalis*.

Results obtained in the biological determination of comparative amounts of polysaccharides in thirty varieties of *Phaseolus vulgaris*, six of *Pisum sativum*, and four of *Ervum lens* show that the use of invertase for this purpose is satisfactory. H. J. E.

New Crystalline Chromogen, Esculetol, extracted from Horse Chestnuts. G. Bertrand and (Miss) Y. Djoritch (*Compt. rend.*, 1924, **178**, 1233—1236).—The authors have isolated from the fruit of the horse chestnut the chromogenic substance which occurs in the envelope of the fruit and is colourless while in the living cells, but under the influence of the laccase present rapidly becomes deep yellow when the cell sap is exposed to the air. This chromogen, named *esculetol*, crystallises from aqueous solution in lustrous, colourless prisms, commonly united in rosettes, and, in a vacuum over sulphuric acid, undergoes dehydration to a powder of irregular lamellæ and slender needles, m. p. (Maquenne block) 275—280°. In the air, it undergoes gradual oxidation and assumes a pink colour, and in aqueous solution it is coloured an intense green by ferric chloride and brownish-yellow by absorption of oxygen or by addition of sodium or potassium hydroxide. It reduces iodic acid and gold chloride in the cold, and silver nitrate and copper acetate when heated. It is not a glucoside, and the extent to which it reduces cupro-potassium solution is not increased by previous treatment with dilute acid. T. H. P.

The Isoelectric Points of some Plant Proteins. W. H. Pearsall and J. Ewing (*Biochem. J.*, 1924, **18**, 329—339).—The examination of a representative series of plant proteins shows that the isoelectric point of these compounds is usually about p_H 4·5 or less often about p_H 3·3. Edestin is the only exception. S. S. Z.

Solanine Content of Potatoes. A. Bömer and H. Mattis (*Z. Unters. Nahr. Genussm.*, 1924, **47**, 97—127).—The methods previously described for determining solanine are subjected to a critical examination. Von Morgenstern's method does not give quantitative results, and the solanine obtained by Meyer's method is on an average only 62·2% pure. The solubility of solanine in ether, acetone, alcohol, and in faintly ammoniacal water has been redetermined. Neither dilute acetic acid, ammonia, nor barium hydroxide decompose solanine appreciably. A simplified method of determining the solanine content of potatoes is given, which gives considerably higher results than that of Meyer or that of von Morgenstern. The original must be consulted for details. The solanine content of a large number of potatoes of various kinds grown under specified conditions as to soil and fertiliser, determined by this method, varied between 2 and 10 mg. %. Potatoes with a content of more than 20 mg. % of solanine appear to be unsafe for consumption. The solanine content of potatoes definitely shown to be prejudicial to health has varied between 25·7 and 58·3 mg. %. Unripe potatoes have a considerably greater con-

tent of solanine than ripe potatoes of the same variety; small potatoes contain more than large ones. An increase in the solanine content occurs on prolonged exposure of potatoes to the light at the same time as the formation of chlorophyll. No connexion could be traced between the use of artificial fertilisers and the solanine content of the potatoes. When potatoes of high solanine content are used as seed, the resulting crop is of normal solanine content, both as regards tops and tubers. H. C. R.

Surface Tension of Saponin Solutions. H. WASTL.—(See ii, 462.)

Comparative Plant Chemistry. IX. Chemistry of Barks. I. C. FEINBERG, J. HERRMANN, L. RÖGLSPERGER, and J. ZELLNER (*Monatsh.*, 1924, **44**, 261—276).—Young barks of three species of trees were examined: (1) Field maple (*Acer campestre*, L.); this contained: soluble in light petroleum, 0·56%; ether extract, 1·12%; alcoholic extract, 9·34%; total water-soluble matters, 15·65%; water-soluble mineral matters, 1·11%; tannin, 4·00%; phlobaphens, 3·00%; free acids (as KOH), 1·12%; reducing sugars, trace; sucrose, 1·09%; polysaccharides, 0·55%; total nitrogen, 2·05%; total ash, 11·27%. The light-petroleum extract contained a *phytosterol*, m. p. 128°, $[\alpha]$ −24·7°, and hydrolysis of the fats yielded ceryl alcohol, arachidic acid, and a mixture of other acids. The ether extract contained an *octadecyl alcohol*, m. p. 75°. The tannin, of the approximate formula $(C_{10}H_{12}O_5)_n$, gave protocatechuic acid on fusion with alkali.

(2) Hazel (*Corylus Avellana*, L.) contained: soluble in light petroleum, 4·25%; ether-soluble, 3·45%; alcohol-soluble, 9·34%; total water-soluble, 15·06%; reducing sugars, 2·61%; tannin, 5·23%; free acids (as KOH), 3·96%; polysaccharides, 1·36%; soluble mineral matter, 0·94%; total nitrogen, 0·60%; crude fibre, 48·04%; total ash, 5·97%. The light-petroleum fraction yielded a new substance, $C_{34}H_{60}O_2$, termed *corylol*, colourless needles from alcohol, m. p. 240° (decomp.), which gave a cholestol reaction (*acetyl* derivative, m. p. 102°; *benzoyl* derivative, m. p. 136°; *acetylbromo* derivative, m. p. 115°). Corylol is similar to, but not identical with alnulin (*vide infra*), cerin, and friedelin (cf. Istrati and Ostrogovitch, A., 1899, i, 772); the light-petroleum fraction also yielded a *substance* ($C_{20}H_{36}O_2$), m. p. 199—200°, which gave a cholestol reaction, and a *wax-alcohol*, m. p. 75°. The ether extract gave a *resin acid*, m. p. 272°, and a *substance* crystallising in needles ($C_{35}H_{60}O_4$?), m. p. 254° (*acetyl* derivative, m. p. 215°), named *coryliresinol*, similar to but differing definitely from corylol.

(3) Grey alder (*Alnus incana*, L.) contained: soluble in light petroleum, 8·97%; ether-soluble, 2·91%; alcohol-soluble, 17·32%; tannins, 9·76%; total water-soluble matters, 27·03%; free acids (as KOH), 1·23%; polysaccharides, 3·15%; total nitrogen, 1·26%; total ash, 2·00%. The light-petroleum fraction afforded long, colourless needles of a substance ($C_{35}H_{60}O$?) termed *alnulin*, m. p. 261° (decomp.) (*acetyl* derivative, m. p. 237°; *bromine additive*

product, m. p. 210°). A second crystalline product was also isolated, termed *alniresinol* ($C_{34}H_{58}O_3$?), m. p. 179° (decomp.), which gave a cholestol reaction, *acetyl* derivative, needles, m. p. 258°; it appears to be a resin alcohol. Traces of a third *substance*, $C_{34}H_{60}O_3$, were also obtained, m. p. 210°. F. A. M.

Chemical Composition of the Clandestine. A. GORIS (*Compt. rend.*, 1924, **178**, 1203—1205).—The glucoside, clandestinin, of *Lathrea clandestina*, the extraction of which is described, appears to be identical with meliatin. H. J. E.

Comparative Plant Chemistry. VIII. *Chamænerium angustifolium*. K. PÜRINGER (*Monatsh.*, 1924, **44**, 255—260).—The leaves and flowers were examined separately, giving the following results (figures for flowers in brackets): soluble in light petroleum, 4·82% (2·76%); in ether, 4·20% (5·39%); in alcohol, 15·61% (19·77%); total water-soluble, 37·45% (41·04%); water-soluble mineral matter, 5·23% (6·05%); free acids (as KOH), 2·46% (5·32%); reducing sugars, 5·27% (8·47%); tannin, 12·15% (12·67%); phlobaphen, 1·07% (—); total nitrogen, 2·47% (2·26%); protein nitrogen, 2·02% (—); crude fibre, 10·54% (13·53%); ash, 7·70% (6·73%). The general results resemble those obtained with *Knautia* (cf. this vol., i, 816). The plant is used in Russia for adulterating tea. The ether extract contained an amorphous white *substance*, m. p. 256—260° (decomp.), $[\alpha]$ +72·75° in alcohol, which forms an *iodine additive* product, m. p. 118—120°, and an *acetyl* derivative, m. p. 178—180°; it is probably a resin alcohol. The alcoholic plant extract contained small amounts of choline and invert-sugar. F. A. M.

Tissue Fluids of Egyptian and Upland Cottons and their F_1 Hybrid. J. A. HARRIS, Z. W. LAWRENCE, W. F. HOFFMAN, J. V. LAWRENCE, and A. T. VALENTINE (*J. Agric. Res.*, 1924, **27**, 267—328).—The osmotic concentration of the leaf-tissue fluid, as measured by the freezing-point depression, is slightly but definitely greater in Egyptian than in Upland cottons. The electrical conductivity and acidity are also greater in the Egyptian cotton; the average p_H values varies from 5·26 to 5·40. The osmotic concentration and electrical conductivity are lower in the hybrid than in either of the parents, but the hydrogen-ion concentration falls between those of the parents. As the season advances, the concentrations of total solutes, ionised solutes, and hydrogen ions decrease whilst the differences between the various types of cotton become more marked. Soil conditions and atmospheric conditions during the period of sampling exert a marked influence on the values; the concentration of total solutes is most affected by these environmental factors. E. M. C.

Histological and Chemical Examination of the Seeds of *Ipomœa hederacea*, Jacquin, and of other Species of *Ipomœa*. H. C. KASSNER (*Pharm. J.*, 1924, **112**, 328—331, 357—359).—The seeds of *Ipomœa hederacea*, Jacq., *I. muricata*, Jacq., *I. pes-tigridis*, L.,

I. coccinea, L., *I. pilosa*, Sw., and *I. eriocarpa*, R. Br., all contain a crude resin and a fatty oil as principal constituents. The physical and chemical properties of both these constituents of the different species are given and show that the resins and oils obtained from them were very similar to one another. The seeds of *I. muricata* gave a larger percentage of ether extract after extraction with petroleum spirit, but a smaller quantity of crude resin in the subsequent extraction with alcohol than did those of *I. hederacea*. The seeds of *I. hederacea* contained a larger percentage of the medicinally active resin than those of any of the other species. About 2% of a true resin was isolated from the seeds of *I. hederacea* free from glucosidal matter. The crude resin comprises a mixture of this true resin with a large quantity of glucosidal matter and with a saponin-like substance. Neither the true resin nor the crude resin is identical with convolvulin, the ether-insoluble resin of jalap. The true resin and the crude resin of Kaladana (*I. hederacea*) differ from the jalap and scammony resins in that they are insoluble in ether and give an immediate turbidity on acidifying a boiled alkaline ethereal solution. True Kaladana resin is not precipitated as readily or completely as certain other convolvulaceous resins when its alcoholic solution is poured into water. The true, glucoside-free resin of Kaladana possesses medicinal properties similar to those of jalap resin. The crude resin does not, however, form a wholly satisfactory substitute for jalap resin owing to the presence of a large amount of glucosidal matter which acts as a hygroscopic diluent. The percentage of fatty oils and crude resins in the various species of seeds was 9·23—14·94% and 9·20—15·98%, respectively. *I. coccinea* gave the greatest yield of oil and *I. hederacea* the greatest yield of resin. The monographs on Kaladana in the B.P., 1914, and B.P. Codex, 1923, are inaccurate and need revision. H. C. R.

Chemical Factors determining the Quality of Tobacco. V. Graham and R. H. Carr (*J. Amer. Chem. Soc.*, 1924, **46**, 695—702).—There is a relation between the grades of tobacco and their relative solubilities; a high quality cigar tobacco, for instance, has a lower percentage of extractives and nicotine than has a poorer grade. The irritant effect produced by inferior tobaccos is due to the presence of waxes, volatile oils, and loosely combined nicotine, and it is suggested that the quality could be improved by a preliminary extraction with light petroleum. The quality of the tobacco is not so much altered by the use of fertilisers as by changes in the nature of the soil and climatic conditions; of the fertilisers employed superphosphate was found to have the most marked effect in improving the quality. Plants grown on soil containing much lime contained a considerable amount of nicotine–calcium compounds. The best qualities of tobacco are grown on relatively poor sandy and clay soils unsuited for cereals. C. J. S.

Comparative Plant Chemistry. VII. *Knautia silvatica*. J. Zellner (*Monatsh.*, 1924, **44**, 247—251).—The leaves and

flowers were examined separately and had the following contents (figures for petals in brackets): soluble in light petroleum, 3·21% (2·18%); in ether, 2·13% (3·59%); in alcohol, 25·77% (30·14%); total water-soluble, 40·99% (39·43%); water-soluble mineral matter, 8·27% (6·10%); phlobaphen, 4·68% (6·18%); tannin, 7·80% (6·85%); free acid (as KOH), 2·51% (2·50%); reducing sugars, 4·43% (5·38%); soluble carbohydrates, 4·03% (2·23%); crude fibre, 14·19% (17·37%); pentosans, 7·68% (10·49%); methylpentosans, 1·02% (1·37%); total nitrogen, 1·96% (2·69%); total ash, 13·42% (8·56%). The tannin yielded protocatechuic acid on fusion with potassium hydroxide; invert-sugar and choline were also present in the alcohol extracts from the leaves. The colloidal carbohydrate contained in the aqueous extract yielded mucic acid and furfuraldehyde as degradation products, and is therefore regarded as a galactopentosan. Attention is directed to the similarity in chemical composition of the leaves and petals.

F. A. M.

Chemistry of Heterotropic Phanerogams. IV. J. Einleger, J. Fischer, and J. Zellner (*Monatsh.*, 1924, **44**, 277—295).—Mistletoe (*Viscum album*, L.) gave the following results per 100 parts of dried substance (figures for leaves and young stems are given first and figures for berries in brackets): soluble in light petroleum, 5·13% (5·12%); ether-soluble, 3·26% (2·59%); alcohol extract, —, (41·59%); total water-soluble matter, 37·52% (68·08%); water-soluble mineral matter, 7·79% (5·28%); free acids (as KOH), —, (1·19%); reducing sugars, 0·62% (1·33%); pectins 2·05%; soluble polysaccharides, —, (22·4%); tannin, nil (nil); total nitrogen, 2·30% (2·05%); crude fibre, 20·43% (10·85%); ash, 10·40% (5·51%); soluble pentosans, —, (6·58%); insoluble pentosans, —, (3·47%); methylpentosans, —, (0·89%). A new resin alcohol, *visciresinol*, $C_{15}H_{26}O_2$, decomp. 274—276°, was isolated from the leaves and stem; it adds on bromine and iodine in acetic acid and can be acetylated; choline was present but phlobaphens were absent. The berries contained a viscous product which after hydrolysis gave a *substance* decomposing above 280° (*acetyl* derivative, m. p. 250°), possibly identical with visciresinol; a crystalline *wax-alcohol*, m. p. 71°, was also isolated, and an amorphous resin identical with Reinsch's viscin (cf. *Chem. Zentr.*, 1861, 148).

Loranthus europæus gave the following analysis per 100 parts of dried berries: soluble in light petroleum, 11·38%; ether-soluble, nil; total water-soluble matter, 48·84%; water-soluble mineral matter, 4·28%; free acids (as KOH), 1·44%; reducing sugars, 20·00%; water-soluble polysaccharides, 5·09%; total nitrogen, 2·57%; crude fibre, 15·83%; total ash, 4·60%. The fatty portions of the leaf extracts yielded *loranthyl alcohol*, $C_{24}H_{50}O$, m. p. 71—72° (*acetyl* derivative, m. p. 57—58°, *benzoyl* derivative, m. p. 56—57°). A saturated *hydrocarbon*, $C_{30}H_{62}$, was also isolated, m. p. 65°; carotin and phlobaphens were present. Notable amounts of tannin were present which yielded proto-

catechuic acid on alkali fusion. The berries after extraction and hydrolysis yielded cetyl alcohol; an amorphous *resin*, $(C_{10}H_{18}O)_x$, was also obtained, m. p. 65—66°, $[\alpha]$ +14·5°, giving an *acetyl* derivative, m. p. 70—72°. A comparison of the stems of the parasites and their hosts confirmed the results previously found in other cases (cf. Zellner, A., 1920, i, 131) that the parasites had a higher water-content and contained more free acids and soluble nitrogenous compounds than the host, but considerably less reducing sugars. F. A. M.

Microbiological Analysis of Soil as an Index of Soil Fertility. VII. Carbon Dioxide Evolution. S. A. WAKSMAN and R. L. STARKEY (*Soil Sci.*, 1924, **17**, 141—161).—Methods are described for the measurement of carbon dioxide production in soil. The rate at which soils produce carbon dioxide is suggested as a basis on which soils may be classified, both as to fertility and to number of micro-organisms present. For normal soils, carbon dioxide production was greatest where the percentage of organic matter was high, although no direct proportionality was observed. The rate of evolution of carbon dioxide from acid soils was increased by liming, and in these cases nitrification was increased to an even greater extent. A. G. P.

Oxidation of Ammonia and Nitrites by Micro-organisms under Different Conditions. R. N. GAWDA (*Soil Sci.*, 1924, **17**, 57—63).—Marked increases in the rates of oxidation of sodium nitrite and ammonium sulphate in culture solutions of nitrifying organisms were observed when an air current was drawn through the liquid. This rate was further considerably increased by allowing the solution to drip through a column of broken limestone on the surface of which a culture of the organisms was established and through which an air current was passed. Nitrite-bacteria were most active in media with p_H 8·0 and nitrate-forming organisms with p_H 8·5—8·8. Magnesium carbonate used as a base during ammonia oxidation proved devoid of toxic effects. A. G. P.

Sulphur Oxidation in Oregon Soils. W. V. HALVERSEN and W. B. BOLLEN (*Soil Sci.*, 1923, **16**, 479—490).—Attempts to correlate factors concerned in the use of sulphur as a fertiliser are described. An approximate proportionality was found between the sulphur-oxidising power of soils and their sulphate contents. The total sulphur content of soils bore no apparent relationship to either the sulphur-oxidising power or the sulphate content. The rate of sulphur-oxidation can be increased by a previous treatment with sulphur and by the use of inoculated sulphur. Oxidation was favoured by aëration and temperature increases. In heavy soils with high buffer capacities, sulphur oxidation was considerably slower than in light sandy soils having small buffer capacity. The sulphur-oxidising power of a soil was in no way connected with its hydrogen-ion concentration. A. G. P.

Biochemical Conditions of a Soil treated with Different Organic Manures. E. HASELHOFF and O. LIEHR (*Landw. Versuchs.-Stat.*, 1924, **102**, 43—59). **Carbon Dioxide Content of the Soil Atmosphere.** E. HASELHOFF and O. LIEHR (*ibid.*, 60—72). **Nitrogen Economy of Arable Soil.** E. HASELHOFF (*ibid.*, 73—89). **Ammonia and Nitric Acid Content of the Soil.** E. HASELHOFF and F. HAUN (*ibid.*, 90—103). **Effect of Fallow, Dung, and Green Manures in Conjunction with Mineral Manures.** E. HASELHOFF (*ibid.*, 104—121).—This series of papers contains a detailed discussion of an investigation of the soil from a large number of plots, over a period of 10 years, on which a rotation of wheat, potatoes, rye, and oats followed green manuring with serradella, peas, and clover. Other plots received dung or were fallowed. The whole rotation was repeated twice. Determinations are recorded of bacterial numbers, and ammonifying, nitrifying, and nitrogen-fixing powers of soil samples; the carbon dioxide content of the soil atmosphere at depths of 25 and 50 cm.; the total nitrogen recovered in the crops; the ammonia and nitric acid of the soil, as determined colorimetrically in aqueous extracts; and the crop yields with green manures and ammonium sulphate. Reference should be made to the original papers, since the results do not allow any definite conclusions to be given briefly.

E. M. C.

Moisture Relationships in an Ideal Soil. B. A. KEEN (*J. Agric. Sci.*, 1924, **14**, 170—177).—The views of a number of soil physicists are discussed in a theoretical paper, on the basis of the mathematical relationships of soil and water in an ideal soil.

A. G. P.

Imbibitional Soil Moisture. E. A. FISHER (*J. Agric. Sci.*, 1924, **14**, 204—220).—In continuation of former papers (see *Ann. Repts.*, 1923, **20**, 202), the nature of imbibitional or "gel" water is discussed, particularly in respect of its effect on the movement of water in soils. The imbibitional process may be due to the attainment of a Donnan equilibrium within the "swollen" colloidal particles of the soil. The possible effects of imbibition on the movement of soil-water are discussed mathematically. A. G. P.

Measurement of Hydrogen-ion Concentration in Soil by means of the Quinhydrone Electrode. E. BILLMANN (*J. Agric. Sci.*, 1924, **14**, 232—239).—Apparatus is described for the determination of hydrogen-ion concentrations of soil–water suspensions by means of an electrode vessel containing quinhydrone as the source of hydrogen. Rapid equilibrium is attained, and the results are in close agreement with those yielded by the colorimetric method and the standard hydrogen electrode. A. G. P.

Electrical Conductivity of Extracts from Soils of Various Types and its Use in Detecting Infertility. W. R. G. ATKINS (*J. Agric. Sci.*, 1924, **14**, 198—203).—The electrical conductivity of

aqueous soil extracts increased with the period of extraction in the case of rich soils, but reached its maximum quickly in the case of infertile soils and peats. High conductivity does not necessarily indicate a good soil, but a rapid increase with extended extraction period appears to be characteristic of fertility. A. G. P.

Modifications in Soil Dried in the Air. A. LEBEDIANTZEV (*Compt. rend.*, 1924, **178**, 960—963).—The proportions of organic matter, total nitrogen, and ammoniacal nitrogen extractable from soil by water and acid solutions are greatly increased by preliminary drying of the soil in the air. At the same time, the extractable phosphoric acid increases appreciably and the extractable mineral matter slightly, whilst the bacteria present undergo considerable diminution. These effects are due, not to the action of oxygen or light, but to the loss of water and to the rise of temperature caused by the sun's rays. T. H. P.

Determination of Carbonic Acid present as Carbonate in Soils. P. B. SANYOL (*Agric. Res. Inst. Pusa, Bull.* No. 151).—Carbonates in the soil are decomposed by treatment with cold hydrochloric acid in a vessel containing a stirrer. When no more gas is evolved the carbon dioxide dissolved in the liquid is completely driven out by the generation of hydrogen from aluminium foil. The rate of hydrogen generation is regulated by the addition of a copper sulphate solution. A. G. P.

Calcium Content of Soil in Relation to Absolute Reaction. C. O. SWANSON, P. L. GAINEY, and W. L. LATSHAW (*Soil Sci.*, 1924, **17**, 181—191).—Analyses of a large number of soils indicate that in similar types of soil a close relationship exists between the p_H value of the soil and the amount of calcium present in a form soluble in cold *N*-hydrochloric acid solution. A. G. P.

Adsorption and Absorption of Bases by Soils. C. P. JONES (*Soil Sci.*, 1924, **17**, 255—273).—Experiments are described in support of the view that the adsorption of bases by soil colloids is but a preliminary or accessory factor to the absorption of bases, which is a chemical reaction between the soil constituents and added substances. The latter phenomenon is considered of the greater importance and is governed by the chemical nature of the reactive soil constituents and by those factors limiting the extent of the hydrolysis of the reacting substance. The absorption of basic ions is greater as the degree of ionisation decreases. The absorption of the base of sparingly soluble substances is dependent on their fineness of division. A. G. P.